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AN ASSESSMENT OF GAS-SIDE FOULING IN CEMENT PLANTS

By  
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Pasadena, California

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# An Assessment of Gas-Side Fouling in Cement Plants

W.J. Marner

September 1982

Prepared for  
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## ABSTRACT

The cement industry is the most energy-intensive industry in the United States in terms of energy cost as a percentage of the total product cost. The purpose of this study is to provide an assessment of gas-side fouling in cement plants with special emphasis on heat recovery applications. In the present context, fouling is defined as the buildup of scale on a heat-transfer surface which retards the transfer of heat and includes the related problems of erosion and corrosion. Exhaust gases in the cement industry which are suitable for heat recovery range in temperature from about 400 to 1300 K, are generally dusty, may be highly abrasive, and are often heavily laden with alkalies, sulfates, and chlorides. Particulates in the exhaust streams range in size from molecular to about 100  $\mu\text{m}$  in diameter and come from both the raw feed as well as the ash in the coal which is the primary fuel used in the cement industry. The major types of heat-transfer equipment used in the cement industry include preheaters, gas-to-air heat exchangers, waste heat boilers, and clinker coolers. At the present time, the trend in this country is toward suspension preheater systems, in which the raw feed is heated by direct contact with the hot kiln exit gases, and away from waste heat boilers as the principal method of heat recovery. The most important gas-side fouling mechanisms in the cement industry are those due to particulate, chemical reaction, and corrosion fouling. Particulate transport mechanisms which appear to be of greatest importance include laminar and turbulent mass transfer, thermophoresis, electrophoresis, and inertial impaction. Chemical reaction mechanisms of particular importance include the deposition of alkali sulfates, alkali chlorides, spurrite, calcium carbonate, and calcium sulfate. At sufficiently low temperatures, sulfuric acid and water can condense on heat exchanger surfaces which can cause corrosion and also attract particulates in the flow. The deleterious effects of gas-side fouling in cement plants are due to: (1) increased capital costs, (2) increased maintenance costs, (3) loss of production, and (4) energy losses. A conservative order-of-magnitude analysis shows that the cost of gas-side fouling in U.S. cement plants is \$0.24 billion annually. Recommendations for further work in the area of gas-side fouling in cement plants include a comprehensive study of gas-side fouling mechanisms, as well as several other prioritized short-term and long-term projects.

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## NOMENCLATURE

$A$	constant in Eq. 5-23
$A_0$	constant in Eq. 5-7
$B$	constant in Figure 5-3
$B_0$	constant in Eq. 5-24
$c$	particle concentration
$d_p$	particle diameter
$D$	diffusion coefficient
$E$	activation energy
$f$	friction factor
$J$	particle mass flux
$k_g$	gas thermal conductivity
$k_p$	particle thermal conductivity
$k_t$	transport coefficient of the particles near the surface
$m_p$	particle mass
$p$	sticking probability
$Pr$	Prandtl number
$q$	electrical charge
$R$	gas constant
$R_f$	fouling resistance
$R_f^*$	asymptotic fouling resistance
$Re_p$	particle Reynolds number
$Sc$	Schmidt number
$S$	stopping distance
$S^+$	dimensionless stopping distance
$t$	time
$V$	fluid velocity

$V_p$	particle velocity
$V_t$	thermophoretic particle velocity
$V_{pn}$	particle velocity normal to surface
$x$	ratio of observed to predicted deposition coefficient with $p = 1$
$y$	spatial coordinate normal to surface
$\alpha$	coefficient defined by Eq. 5-3
$\nabla T$	temperature gradient
$\epsilon$	eddy diffusivity for turbulent mass transfer
$\epsilon_0$	permittivity in free space
$\mu$	gas viscosity
$\nu$	gas kinematic viscosity
$\rho_p$	particle density
$\tau_w$	wall shear stress
$\Phi_d$	fouling deposition rate
$\Phi_r$	fouling removal rate
$\Psi$	fouling deposit strength



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## SECTION 1

### INTRODUCTION

Heat recovery from medium and high temperature exhaust gas streams is essential for the efficient operation of most industrial energy conversion systems. However, in many instances such gases are dirty, contain corrosive components, and are laden with particulates which results in severe gas-side fouling problems. In the present context, fouling may be defined as the buildup of scale on a heat exchanger surface which retards the transfer of heat and includes the associated problems of corrosion and erosion. Although gas-side fouling has been identified as a major problem in heat-recovery systems, inadequate research has been done in this area. The purpose of the present study is to assess the state-of-the-art of gas-side fouling in an important heat-recovery environment, namely cement plant exhausts. At the present time, the cement industry is the most energy-intensive industry in the United States in terms of energy cost as a percentage of the total product cost (Reference 1-1).

The major objectives of this study are:

- (1) Characterize the waste heat exhaust streams in cement plants as to: type of fuel, chemical composition including particulates, temperature, and flow rate.
- (2) Determine past and present experience with various types of heat-recovery equipment in cement plants and evaluate the associated gas-side fouling problems.
- (3) Identify and attempt to quantify the deleterious effects of gas-side fouling in cement plants including increased energy consumption, increased material losses, and the loss of production.

- (4) Recommend a well-defined R&D program for gas-side fouling in cement plants which includes both short-term and long-term applied research projects.

The information described above was obtained through a literature survey, personal contacts, and visits to selected industries in the cement industry. Visits were made to Smith Engineering Company, Duarte, California, Riverside Cement Company, Oro Grande, California, and the Portland Cement Association, Skokie, Illinois. In addition, the author attended the 17th International Cement Seminar which was held in Chicago, Illinois, on December 6-9, 1981. Attendance at this Seminar afforded a broad exposure to cement-industry technology and the opportunity for personal interactions with a number of representatives from the cement industry.

## SECTION 2

### THE MANUFACTURE OF PORTLAND CEMENT

Although the use of cement dates back to antiquity, the portland cement industry as it is known today apparently started in 1824. In that year Joseph Aspdin, an Englishman, patented an artificial cement made by the calcination of an argillaceous limestone. He called this portland because concrete made from it resembled a famous building stone obtained from the Isle of Portland near England (Reference 2-1).

Portland cement is made by mixing and calcining (heating to a high temperature to drive off volatile matter) materials which contain limestone, silica, alumina, and iron oxide, in the proper proportions, to a temperature between 1725 and 1875 K. ASTM has defined portland cement as (Reference 2-2):

a hydraulic cement produced by pulverizing  
clinker consisting of hydraulic calcium  
silicates, usually containing one or more  
forms of calcium sulfate as an interground  
additive.

Eight types of portland cement are recognized in the United States depending on the varying amounts of the clinker compounds listed in Table 2-1 and the addition of air-entraining agents. As may be seen from Table 2-1, lime compounds of silica, alumina, and iron account for all but a small fraction of the constituents of portland cement clinker.

Heating of the finely-ground feed takes place in a rotary kiln as shown in Figure 2-1. The kiln consists of a large cylindrical shell, which is lined with firebrick, typically with a diameter of 2.13 to 7.32 m. The kiln

Table 2-1. Portland Cement Clinker Compounds (Reference 2-1)

Name	Formula	Abbreviation
Dicalcium Silicate	$2\text{CaO} \cdot \text{SiO}_2$	$\text{C}_2\text{S}$
Tricalcium Silicate	$3\text{CaO} \cdot \text{SiO}_2$	$\text{C}_3\text{S}$
Tricalcium Aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	$\text{C}_3\text{A}$
Tetracalcium Aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	$\text{C}_4\text{AF}$
Magnesium Oxide in Free State	$\text{MgO}$	$\text{MgO}$

axis is inclined at a slight angle with the horizontal, typically 20.8 to 83.2 mm per m. The kiln is driven through a spur pinion meshing with a large girth gear and rotates slowly on the order of 1 to 3.5 rpm. The raw feed is introduced at the upper end of the kiln and heat is supplied at the lower end of the kiln by a hot flame. Thus, the hot combusted gases flow in a countercurrent direction to the feed in the kiln.

As the raw material, typically occupying 7 to 8 percent of the kiln volume, moves through the kiln under the rotary action of the kiln, a series of chemical changes take place which produce the formation of marble-sized clinker. The most important reactions which take place in the kiln, and the temperatures at which they occur, are given in Table 2-2. (Reference 2-3). At the exit of the kiln, the clinker which is at a temperature of about 1775 K, passes through a clinker cooler where it is cooled by ambient air. Portland cement is then made by grinding the clinker very finely and mixing it with up to five percent gypsum (calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to control the set of the cement.



Table 2-2. Reactions in the Cement Kiln and the Temperature Ranges at Which They Occur (Reference 2-3)

Reaction	Temperature Range, K
Evaporation of Free Water	375-395
Evolution of Combined Water	Up to 775
Evolution of $\text{CO}_3$ from Limestone (Calcination)	1075-1125
Formation of $\text{C}_3\text{S}$	1075-1175
Formation of $\text{C}_3\text{A}$ and $\text{C}_4\text{AF}$	1370-1480
Formation of $\text{C}_3\text{S}$	1535-1730

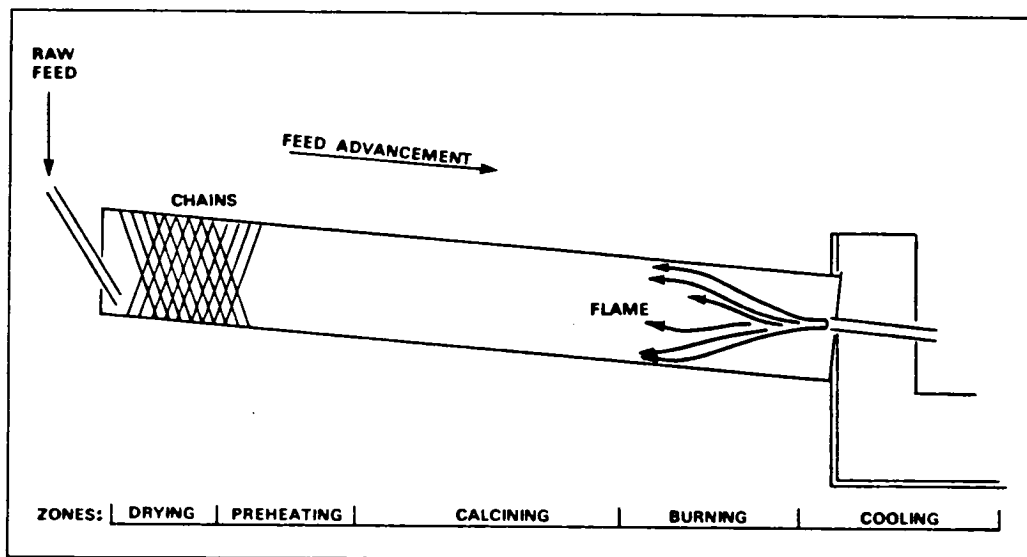


Figure 2-1. Schematic Drawing of Kiln Used in Cement Manufacturing by Simple Wet and Dry Processes (Reference 2-3)

In the United States two basic processes, the wet process and the long-dry process, are used to make portland cement. In addition, two variations of the long-dry process are becoming increasingly popular. Therefore, the four types of processes are:

- (1) Wet process.
- (2) Long-dry process.
- (3) Suspension preheater dry process.
- (4) Suspension preheater/precalciner combination process.

In the wet process the raw materials are proportioned, ground with water, blended, and fed into the kiln as a slurry. In the dry process the raw materials are dried, proportioned, ground, blended, and fed into the kiln essentially as a dry mixture. In the wet process the slurry encounters a system of chains which are attached to the surface of the kiln. As the kiln rotates, the chains become coated with the slurry and heat is transferred from the hot combustion gases which dries the raw feed. The raw mix is then converted to nodules which move down the kiln through the preheater, calcining, and burning zones as shown in Figure 2-1. On the other hand, in the dry process very little drying is required before the raw feed passes through a mixing device -- such as chains, lifters, or trefoils -- prior to moving through the calcining and burning zones.

Although there are several types of preheaters, the trend is toward the use of suspension preheaters, so-called because the raw feed particles are suspended in a series of cyclones, usually four, in which the feed moves in a countercurrent flow to the upward moving exhaust gases. Thus, the suspension preheater provides for a direct contact heat transfer mechanism between the hot kiln exhaust gases and the cold feed. A typical arrangement of a four-cyclone unit for a Fuller-Humboldt preheater is shown in Figure 2-2. As shown, a sequence of suspension and separation is repeated through each cyclone until the preheated, partially calcined feed enters the kiln at about 1075 K where calcination and the burning stages are completed.

A fairly recent innovation is the addition of a precalciner to the suspension preheater, accomplished by introducing an auxiliary fuel burning chamber in the final stages of the preheater, designated by the letters "PC" as

as shown in Figure 2-2. A suspension preheater with four cyclone stages will accomplish about 50 percent of the preheating and calcining of the raw feed before it enters the kiln. Introduction of a precalciner will increase this process to about 90 percent. Thus, in addition to recovering energy from the kiln exhaust gases, the use of preheaters and precalciners allow for a much shorter and smaller diameter kiln for any given capacity.

Also shown in Figure 2-2 is a bypass at the kiln gas flow exit just below the suspension preheater system. The purpose of this bypass, frequently called the alkali or kiln bypass, is to limit the levels of chloride, alkalies, and sulfur in the kiln feed. Typically, the quantity of hot gases which are bypassed around the preheater ranges from 5 to 25 percent, depending upon the rate of feed, gas flowrate, and specific operating conditions.

A summary of the number of cement plants operating in the United States during 1980 is given in Table 2-3, categorized according to the type of process. This table was constructed from data given in Reference 2-4. Although the number of wet and dry kilns is about equal at the present time, the trend is away from wet kilns and toward dry kilns because the latter are more efficient from an overall energy standpoint. In 1973, 58 percent of the kilns were of the wet process type. At that time only five percent of the long-dry process kilns utilized preheaters compared to 23.3 percent in 1980. Also, the trend in the United States is toward fewer, but larger, cement kilns. In 1980 there were 327 kilns, a reduction of 26.5 percent compared to the 445 kilns which were in existence in 1973. However, the annual clinker capacity of 86,337,000 short tons in 1980 was 1.4 percent greater than in 1973, even though there were 118 fewer kilns. In the cement industry the short ton is widely used as a measure of weight:  $1 \text{ short ton} = 2000 \text{ lb}_m = 0.907 \text{ metric ton}$ .

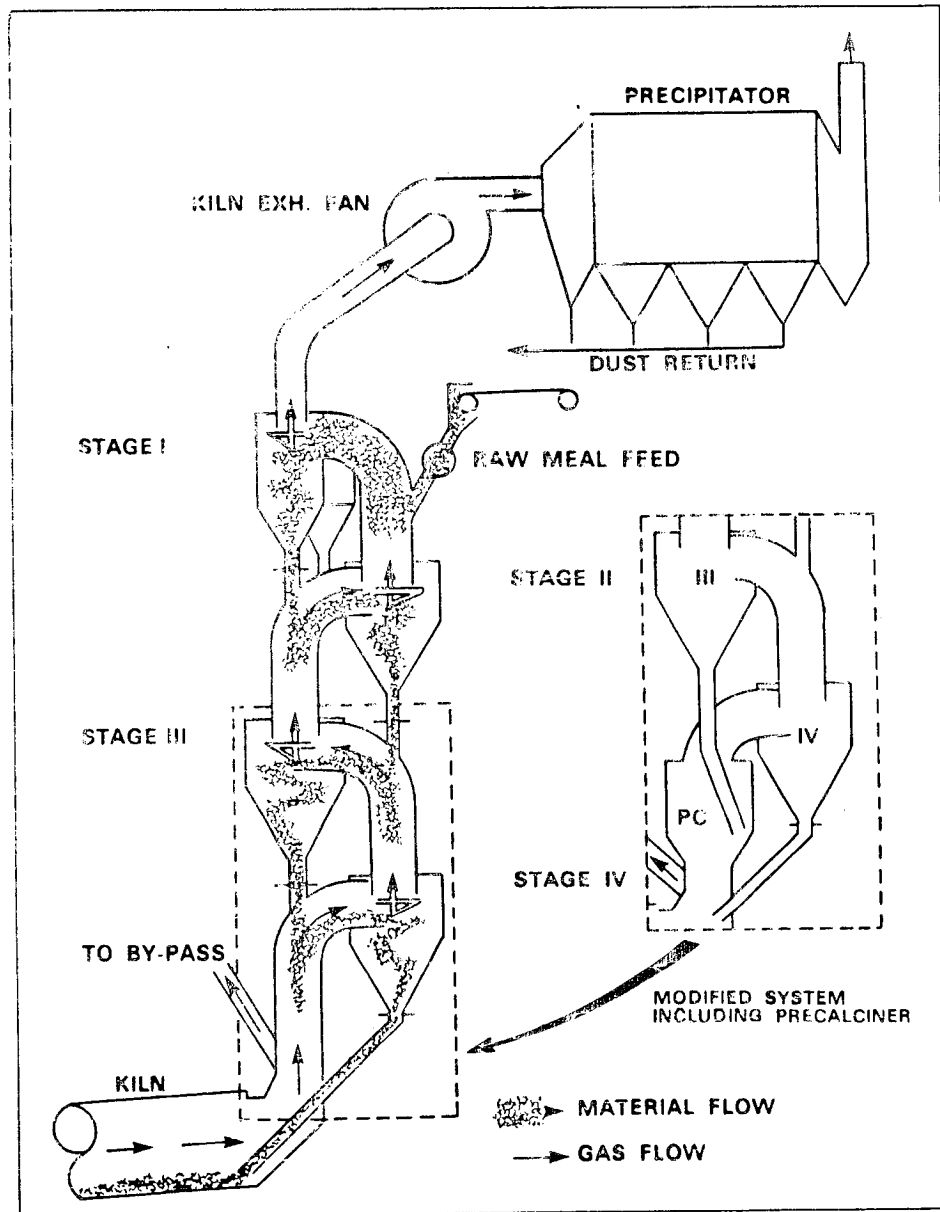


Figure 2-2. Fuller-Humboldt Suspension Preheater with and without Precalciner (Reference 2-3)

Table 2-3. Summary of Cement Plants Operating in U.S.  
during 1980 (Reference 2-4)

Process	Number of Kilns	Annual Clinker Capacity (1,000 Short Tons*)	Percent of Total Annual Capacity
Wet	175	42,564	49.3
Long-Dry	104	23,613	27.4
Preheater**	48	20,160	23.2
Total	327	86,337	100.0

\* 1 short ton = 2000 lb<sub>m</sub> = 0.907 metric ton

\*\* Includes eleven combination preheater-precalciner systems with an annual clinker capacity of 7078 (1,000 Short Tons).



## SECTION 3

### CHARACTERIZATION OF WASTE HEAT EXHAUST STREAMS IN CEMENT PLANTS

The purpose of this section is to characterize the various waste heat exhaust streams in cement plants. Basically, the quantity and quality of exhaust gases in cement plants depends on a number of factors including the:

- (1) Type of fuel.
- (2) Fuel rate in the kiln and precalciner.
- (3) Composition of the raw materials.
- (4) Quantity of excess air.
- (5) Heat transfer processes within the kiln.
- (6) Amount of water, if any, in the raw materials.
- (7) Specific process which produces the exhaust gas stream.

From the standpoint of heat recovery and the associated gas-side fouling problems, the specific parameters of interest include the type of fuel, the composition of the raw materials, the volumetric flowrate and temperature of the various exhaust gas streams, and the chemical composition of the various exhaust gas streams, including the particle density and size distribution.

#### 3.1 TYPE OF FUEL

The primary and alternate fuels used in cement plants in the United States during the 1980 calendar year are given in Table 3-1. Based on this data, 87 percent of the plants in this country use coal as the primary fuel at the present time. Only 10 percent use natural gas as the primary fuel and only one percent use oil. With the cost of oil and natural gas increasing far more rapidly than coal, it is expected that this trend toward coal in the cement industry will continue. In addition to these major fuels, there is also some interest in using a variety of waste materials as kiln fuel (Reference 3-1). Included in this category are such fuels as: waste lube oil, wood chips and

Table 3-1. Summary of Fuels Used in Cement Plants in U.S.  
in 1980 (Reference 2-4)

Fuel Type	Primary Fuel			Alternate Fuel		
	Number of Plants	Clinker Capacity (1000 Ton)	Percent of Total Capacity	Number of Plants	Clinker Capacity (1000 Ton)	Percent of Total Capacity
Coal	121	74,724	87	3	1,165	1
Oil	3	1,164	1	22	16,451	19
Natural Gas	12	8,219	10	44	22,794	26
Coal, Oil	0	0	0	1	312	0
Oil, Natural Gas	0	0	0	24	16,916	20
Total	142	86,337	100	94	57,638	66

sawdust, auto tires, acid sludge, and municipal waste. One of the major problems in utilizing such waste materials is the chemical non-uniformity of these sources. Although such waste materials will never account for more than a small fraction of the fuel used in cement kilns, this topic will probably continue to receive some attention in the future.

Since the primary fuel presently being used in U.S. cement plants is coal, with a continuing trend in this direction, the emphasis in this report is placed on coal as the fuel. Coal may be classified according to the four major ranks which are anthracite, bituminous, sub-bituminous, and lignite. Of these four types of coal, the bituminous rank is the most plentiful and the most widely used.



Coal of any rank consists primarily of carbon, with varying amounts of oxygen, hydrogen, nitrogen, sulfur, and ash as indicated in Table 3-2. The presence of sulfur and the various mineral constituents in the ash are ultimately responsible for the fouling, corrosion, and erosion problems which occur after the combustion process. Coal ash typically makes up about 9 to 10 percent of the coal, although this percentage can vary significantly, and consists primarily of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$ , with smaller amounts of  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{SO}_3$  as indicated in Table 3-3. Additional details on the properties and characteristics of coal may be found, for example, in Reference 3-2.

Table 3-2. Ultimate Analysis of Various Ranks of Coal (Reference 3-3)

Rank	Representative Range of Constituents, Percent by Weight					
	Carbon	Oxygen	Hydrogen	Nitrogen	Sulfur	Ash
Anthracite	64.2-94.7	1.8-14.5	0.5-3.9	0.2-1.8	0.3-1.9	7-5-21.8
Bituminous	59.7-90.7	2.3-20.1	4.4-5.7	1.0-1.7	0.8-5.0	5.2-11.7
Sub-Bituminous	50.5-76.0	14.8-35.5	4.6-6.0	0.7-1.5	0.3-1.8	3.6-9.1
Lignite	40.6-70.9	19.4-45.1	4.5-6.9	0.6-1.1	0.9-1.6	5.9-9.4

Table 3-3. Typical Limits of Ash Composition in U.S. Bituminous Coals  
(Reference 3-4)

Constituent	Chemical Formula	Percent
Silica	SiO <sub>2</sub>	20-60
Alumina	Al <sub>2</sub> O <sub>3</sub>	10-35
Ferric Oxide	Fe <sub>2</sub> O <sub>3</sub>	5-35
Calcium Oxide	CaO	1-20
Magnesium Oxide	MgO	0.3-4
Titanium Dioxide	TiO <sub>2</sub>	0.5-2.5
Alkalies (Potassium and Sodium)	Na <sub>2</sub> O, K <sub>2</sub> O	1-4
Sulfur Trioxide	SO <sub>3</sub>	0.1-12

### 3.2 COMPOSITION OF THE RAW MATERIALS

The raw materials used for making portland cement are a mixture of calcareous (containing calcium carbonate) and argillaceous (like or containing clay) in the proper proportions to provide the chemical compositions for burning or sintering. The calcareous materials presently in use include primarily limestone, along with some marl, cement rock, and chalk. The argillaceous materials include clay, shale, blast-furnace slag, and ashes. The principal raw materials used in producing portland cement are given in Table 3-4. The primary constituent is calcium carbonate, typically ranging from 68 to 78 percent, which undergoes calcination according to the reaction



to produce lime, CaO, which is the primary constituent of portland cement. In addition to the principal constituents given in Table 3-4, there are also generally trace amounts of manganese, strontium, titanium, phosphate, and copper.

Table 3-4. Range of Principal Raw Materials Used in Making Portland Cement (Reference 3-5)

Constituent	Chemical Formula	Range, Percent
Silica	$\text{SiO}_2$	11.5-17.0
Alumina	$\text{Al}_2\text{O}_3$	1.6- 5.0
Ferric Oxide	$\text{Fe}_2\text{O}_3$	1.0- 4.0
Calcium Carbonate	$\text{CaCO}_3$	68.0-78.0
Magnesium Oxide	$\text{MgO}$	3.0- 5.5
Alkalies (Potassium and Sodium)	$\text{K}_2\text{O}, \text{Na}_2\text{O}$	0.4- 1.0

### 3.3 TEMPERATURE AND VOLUMETRIC FLOWRATES

The exhaust streams which offer the greatest potential for heat recovery in cement plants are those from the kiln, the preheater, and the clinker cooler. The approximate volumetric flowrates and temperature levels for the long-dry process, wet process, and preheater process are shown in Table 3-5 which was adapted from References 3-6 and 3-7.

In general, exhaust gases from the kiln or preheater exit are dusty but not particularly abrasive. The temperature of the exhaust gases from the wet process is lower than for the long-dry process because of the very high moisture content in the wet-process feed. In the preheater process the exhaust gas temperature of 645 K leaving the preheater is considerably less than that leaving the kiln of the long-dry process because a portion of the energy in the former case is utilized to heat the feed in the preheater.

The gases leaving the clinker cooler are both dusty and extremely abrasive. A portion of these gases is recuperated and used for secondary air in the kiln and the remaining air is vented to the atmosphere through a baghouse.

Many preheater process kilns have a bypass provision as was shown in Figure 2-2. The purpose of this bypass is to remove a portion of the undesirable constituents such as alkalies, sulfates, and chlorides from the

Table 3-5. Summary of Cement Plant Exhaust Gas Streams  
(Adapted from References 3-6 and 3-7)

Process	Exhaust Gas Source	Physical Characteristics	Approximate Volumetric Flowrate, Standard m <sup>3</sup> per short ton of clinker	Approximate Temperature, K	Gas Energy Content,* kW-hr per short ton of clinker
Long-Dry (900 short tons per 24-hour day)	Kiln Exit	Dusty	1810	865	440
	Clinker Cooler	Dust & Highly Abrasive	1980	445	106
Wet (900 short tons per 24-hour day)	Kiln Exit	Dusty	3960	535	380
	Clinker Cooler	Dusty & Highly Abrasive	1130	410	47
Preheater (3,000 short tons per 24-hour day)	Preheater Exit	Dusty	1240	645	176
	Clinker Cooler	Dusty & Highly Abrasive	1980	480	126
	Bypass	Dusty & Highly Contaminated with Alkalies, Sulfates, & Chlorides	140**	1285	56
All Processess	Finish Mill & Separator		960	365	26

\* Reference temperature 289 K

\*\* Bypass flowrate calculated assuming a 10 percent bypass.

system. This removal is achieved by locating the bypass at the top of the kiln, thus allowing the lighter undesirable gases to leave the kiln-preheater system. These gases then enter a quench chamber where ambient air is used to quickly cool the objectionable compounds. Thus, the contaminants pass quickly from the vapor state to the solid state and avoid the undesirable liquid state (Reference 3-8). In most bypass systems the amount of exhaust gas leaving the kiln which is bypassed typically varies from about 5 to 25 percent by volume, or even higher, depending on the level of contaminants. The volumetric flowrate in Table 3-2 has been calculated on the basis of a 10 percent bypass as indicated. The important point with regard to this particular gas stream is the very high temperature level of about 1285 K. For this reason, even though the gases may be highly contaminated, there is considerable interest in trying to recover a portion of the energy from this high-temperature stream.

Finally, the gases leaving the finish mill and separator, where the clinker is finely ground and mixed with gypsum to produce cement, is about 365 K. However, in comparison with the other gas streams available, there is not too much interest in this particular gas stream at the present time because of the very low temperature level.

#### 3.4 CHEMICAL COMPOSITION

The chemical composition of the various exhaust streams is very important. Of course, this will vary from plant to plant, depending especially on the composition of the feed and the type of fuel. The chemical analyses of four typical kiln dusts, taken from Reference 3-9, are given in Table 3-6. The four dusts are designated as high sulfate (Dust H), high chloride (Dust L), low chloride-low sulfate (Dust M), and moderate sulfate (Dust S). The sulfates are characterized by the percentage of  $\text{SO}_3$ , the chlorides by Cl, and the alkalies by  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ . Although the chemical compositions given in Table 3-6 were obtained at room temperature, such data -- in conjunction with additional information -- are necessary in trying to understand the fouling phenomena which occur at elevated temperatures.

Table 3-6. Chemical Analyses of Representative Kiln Dusts  
(Reference 3-9)

Constituent	Kiln Dust Designation			
	H	L	M	S
	Percent by Weight			
SiO <sub>2</sub>	14.6	13.4	11.4	16.4
Al <sub>2</sub> O <sub>3</sub>	4.0	2.66	3.48	2.89
Fe <sub>2</sub> O <sub>3</sub>	2.2	1.25	1.16	2.33
CaO	43.5	37.0	43.2	56.68
MgO	1.23	1.3	1.35	0.85
SO <sub>3</sub>	16.9	2.01	0.73	4.36
Na <sub>2</sub> O	0.39	0.44	0.08	0.07
K <sub>2</sub> O	5.57	10.31	2.22	0.82
P <sub>2</sub> O <sub>5</sub>	0.07	0.19	0.05	0.17
TiO <sub>2</sub>	0.19	0.15	0.16	0.17
LOI	10.20	24.04	35.24	17.86
F	0.21	0.11	0.02	0.1
Cl	0.45	6.24	0.52	0.03

Legend: H = High Sulfate Dust  
L = High Chloride Dust  
M = Low Chloride - Low Sulfate Dust  
S = Moderate Sulfate Dust  
LOI = Loss On Ignition

### 3.5 PARTICLE DENSITY AND SIZE DISTRIBUTION

Two additional parameters which must be given some consideration in the characterization of exhaust gases are: (1) the particle size distribution, and (2) the density of the most important particulates. These parameters are especially important in situations where inertia or momentum effects tend to become dominant.

Although particulates in cement plants can be as large as  $100\text{ }\mu\text{m}$  in diameter, the greatest percentage of them are less than about  $70\text{ }\mu\text{m}$ . Representative particle size distributions are given in Table 3-7 for the most important constituents in the raw feed, bypass, and clinker cooler streams. In Table 3-7, it is seen that both the raw feed and bypass streams have a greater percentage of small diameter particles than the clinker cooler exhaust stream. This fact is apparently one reason why the clinker cooler gases tend to be highly erosive.

The most important particulates in cement kiln dusts are alumina, silica, ferric oxide, and lime, along with smaller amounts of sulfur trioxide and magnesium oxide. The specific gravity and density of these compounds are given in Table 3-8. In heat-recovery applications, the exhaust gas temperature range of interest essentially covers ambient conditions to about  $1075\text{ K}$ . Since the primary gaseous constituent in the exhaust streams is air, the ratio of  $\rho_p/\rho_{\text{air}}$  ranges from about 2000 to 16500 for the constituents given in Table 3-8 under these conditions. This ratio, which is very large, is important in determining the erosion tendencies of the particulates as well as the particle transport to the wall, especially by the mechanism of inertial impaction. Both of these topics will be considered in greater detail in Section 5.

Table 3-7. Representative Particle Size Distributions in Various Cement Plant Streams (References 3-7 and 3-10)

Particle Diameter $\mu\text{m}$	Percentage of Particles With Size Less than Specified Diameter		
	Stream		
	Raw Feed	Bypass	Clinker Cooler
2	9	6	4
5	27	28	17
10	44	50	48
15	53	60	69
20	58	66	78
30	64	74	85
40	68	77	--

Table 3-8. Density of Important Particulates in Cement Kiln Dusts (Reference 3-10)

Constituent	Chemical Symbol	Specific Gravity	Density, $\text{kg/m}^3$
Alumina	$\text{Al}_2\text{O}_3$	3.97	3970
Silica	$\text{SiO}_2$	2.65	2650
Ferric Oxide	$\text{Fe}_2\text{O}_3$	5.24	5240
Lime	$\text{CaO}$	3.32	3320
Magnesium Oxide	$\text{MgO}$	3.58	3580



## SECTION 4

### HEAT-RECOVERY EQUIPMENT USED IN CEMENT PLANTS

The major types of heat-recovery equipment used in cement plants are discussed briefly in this section. Specifically, the following heat exchangers are considered: preheaters, gas-to-air heat exchangers, waste heat boilers, and clinker coolers. The basic function of each type of heat exchanger is reviewed, and some historical perspectives are presented where appropriate. The emphasis is placed on heat-recovery equipment used in U.S. cement plants.

#### 4.1 PREHEATERS

The first rotary cement kiln with a suspension preheater (SP) was put into operation in the U.S. in 1953 at the National Gypsum Company plant in Nazareth, Pennsylvania (Reference 4-1). This system, built by Klockner-Humboldt-Deutz (KHD), was only the fourth such installation in cement plant applications, with the preceding three units located in Germany where the preheater was originally developed. It was marketed in this country by the Fuller Company, Bethlehem, Pennsylvania, as a licensee of KHD, and hence is generally referred to as the Fuller-Humboldt suspension preheater. Thirteen additional units of this type came on stream in the U.S. between 1955 and 1958. However, many difficulties were encountered with these SP units, resulting in the eventual shutdown of about half of them. Major problems occurred due to buildups from alkalies and chlorides and the presence of kerogen (a high-molar-mass combustible material in oil shale) in the raw feed. With the aid of additional operating experience, these problems were eventually overcome by introducing the alkali bypass described in Section 2 and by restricting the SP to those situations in which the raw material did not contain kerogen. Since then, this method of heat recovery used in conjunction with dry-process cement kilns has increased in popularity. At the present time about one-half of the dry-process cement kilns in the United States are equipped with suspension preheaters.

The major impetus, of course, has been provided by the steady rise in energy costs which has placed greater emphasis on effective heat-recovery procedures.

The Fuller-Humboldt SP system, which was shown in Figure 2-2, consists of four cyclones or stages, each of which includes a long riser where the raw feed is introduced and carried upward into the cyclone in parallel flow with the hot gas from the preceding cyclone. Thus, heat is transferred by direct contact between the hot kiln exhaust gases and the cooler raw feed which is held in a state of suspension. Each cyclone thus spins out the feed for gravity discharge into the riser of the next lower cyclone for repeated parallel flow direct contact heat transfer with successively hotter gases. It takes only about 30 s for raw material to pass through the entire preheater during which time it reaches a temperature of about 1075 K and achieves about 45 percent of the total required calcination. In order to withstand temperatures of this magnitude, and to minimize heat losses, most of the steel cyclones, feed pipes, and gas ducts are refractory lined. As might be expected, the pressure drop in suspension preheaters is relatively high, ranging from about 200 to 750 mm water in typical applications.

In addition the Fuller-Humboldt model, there are several other SP types including the Polysius, Miag, and Krupp in Germany and F.L. Smidth in Denmark. Except for the Krupp preheater, the basic principles of operation are similar for each of these preheaters, all of which are shown schematically in Figure 4-1, taken from Reference 4-2. These preheaters, as well as some other models, are described in Reference 4-1. The Krupp system is a counterflow type which includes a pair of cyclones at the top of the preheater. The raw material is fed into the connecting duct as indicated in Figure 4-1, where the gases carry them into the cyclones. The feed then enters the top chamber of the preheater shell and moves counterflow to the exhaust gases to the bottom of the preheater system under the influence of gravity where it enters the kiln. The throat-like constrictions and cone-shaped deflectors insure that no material is entrained upwards and that adequate heat transfer takes place through mixing between the gases and the feed. Although the Krupp preheater has a relatively low pressure

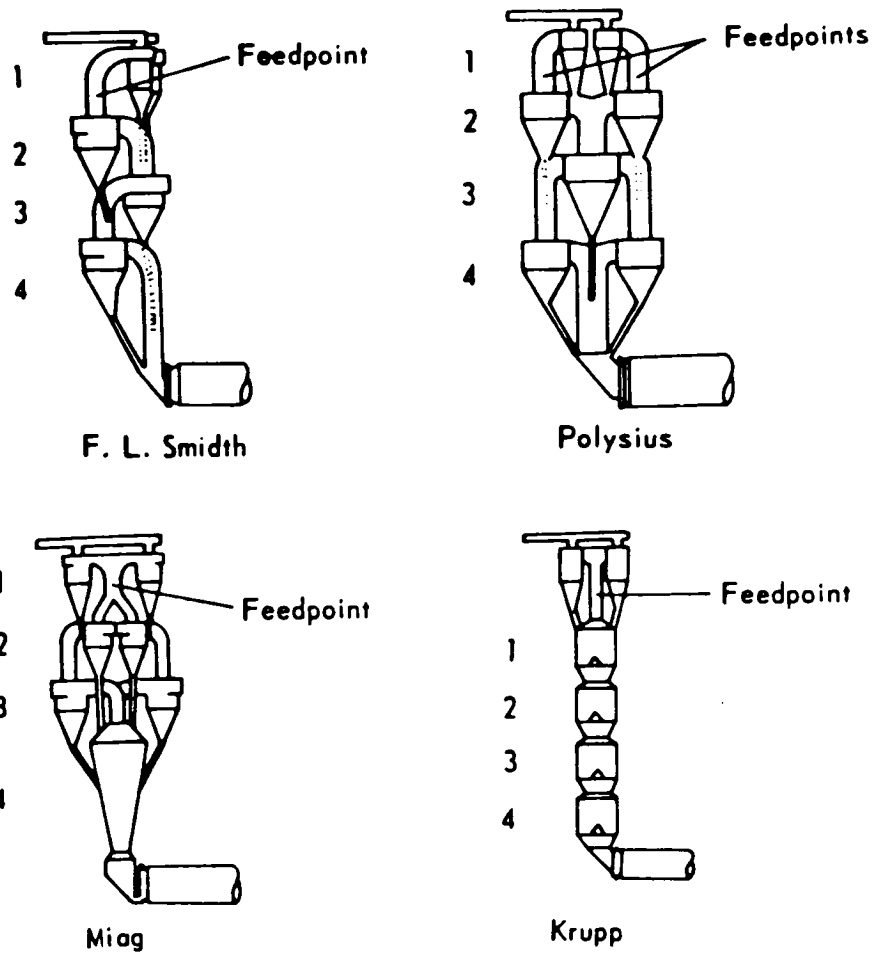


Figure 4-1. Schematic Drawings of the Smidth, Polysius, Krupp, and Miag Suspension Preheaters (Reference 4-2).

drop, as well as a good history of operating experience in Germany, it appears to be less effective from a heat-transfer standpoint, and has not been widely adopted in the U.S. Major reasons for the lack of use in this country include: (1) the absence of an alkali bypass, and (2) no provisions for a precalcining system.

The most recent trend in suspension preheaters is to carry out up to 95 percent of the calcining process in the preheater itself, rather than in the kiln. In such units, since the heat transfer requirements in the kiln are reduced substantially, the kiln size and associated maintenance costs can be reduced significantly. The basic feature of all Secondary Furnace (SF), or precalciner, type kilns is the addition of a separate combustion chamber at the base of the conventional SP system. Combustion in this chamber is generally achieved through the use of multiple burners. Preheated combustion air is provided at a temperature of about 956 K from the clinker cooler as will be discussed in more detail in Section 4.4. Thus, combustion in the precalciner takes place in intimate contact with the preheated suspended raw material. About 60 percent of the total fuel requirements in the SF system are used in the SF chamber itself.

The Fuller-Humboldt preheater with a precalciner has already been shown in Figure 2-2 with the precalciner combustion chamber designated by the initials "PC." A similar unit is being manufactured and marketed by Allis-Chalmers Corporation, Milwaukee, Wisconsin, under a license agreement with Onoda Cement Company, Ltd., Japan. Mitsubishi Mining and Cement Company (Reference 4-3) has recently developed a precalciner with a fluidized bed connected to a conventional suspension preheater. Additional information on suspension preheaters may be found in References 4-4, 4-5, 4-6, and 4-7.

#### 4.2 GAS-TO-AIR HEAT EXCHANGERS

Most of the gas-to-air heat exchangers used in the cement industry in this country are manufactured by Smith Engineering Company, Duarte, California. These exchangers are primarily used to: (1) cool waste heat gases from the preheater or bypass to a temperature of 535 K or lower prior to entering a baghouse where dust and particulates are filtered from the system, and (2) cool clinker cooler vent exhaust gases to a temperature of about 340 K on a recirculating basis or to a temperature of about 480 K for baghouse applications.

In these crossflow exchangers the typically 0.0762 m diameter carbon or stainless steel plain tubes are oriented vertically on an inline layout with longitudinal pitch less than the transverse pitch. The hot, dirty gases are placed on the tubeside for cleaning purposes, if necessary. The heat transfer is effected by blowing ambient air across the outside of the tubes using large fans. A replaceable sleeve, five tube diameters long, is placed in the inlet of each tube to handle erosion problems. These inserts are especially important in clinker cooler applications where the exhaust gases are highly abrasive. These gas-to-air heat exchangers are very large with the tubes typically 6.1 to 12.1 m in length.

In those applications where the primary function of the exchangers is to cool hot exhaust gases, the use of water quenching and bleed-in air is eliminated resulting in a smaller baghouse and hence a smaller system of fans because the exchanger can handle the sharp temperature increases which can occur during upset conditions. Thus, significant savings in energy can be achieved because the reduced air volume requirement results in lower power consumption by the fans.

#### 4.3 WASTE HEAT BOILERS

Waste heat boilers may potentially be used to advantage by utilizing kiln exhaust gases in plants using the wet process or the long-dry process without a preheater system. The incentives are especially attractive in those areas where the cost of electrical power is high. Although the cement industry generated a significant portion of its electrical power requirements in the past using waste heat boilers, the trend in recent years has been toward dry-process suspension preheater systems and away from waste heat boilers.

The following account of the development of steam waste heat boilers in the cement industry is taken from Witt (Reference 4-8). Waste heat boilers were apparently first used in U.S. cement plants at the Nazareth Cement Company, Nazareth, Pennsylvania, in 1897. At that facility the boilers were placed immediately over the rear kiln housing so that the dust-laden gases entered

the boiler directly after leaving the kiln. However, it was impossible to keep the boiler tubes clean under this arrangement, and eventually the boilers were removed. Similar experiences were encountered at the Cayuga Lake Cement Company, Ithaca, New York, and at the Kosmos Portland Cement Company, Louisville, Kentucky. After these unsuccessful attempts, the idea of using waste heat boilers in cement plants was dropped for several years. However, by 1915 several cement manufacturers -- including the Louisville Cement Company, the Sandusky Portland Cement Company, and the Burt Portland Cement Company -- had installed relatively successful waste heat boiler systems. Based on the earlier operating experiences, several modifications were made which improved the performance of the boilers, including: (1) removing some of the dust before the gases entered the boilers, (2) providing soot blowers to keep the boiler tubes clean, and (3) increasing the gas velocity by using induced draft fans rather than stacks. Also, it was at about this time that attention was focused on the problem of air infiltration between the kiln and the boiler which lowered the exhaust gas temperature, and hence the thermal efficiency of the boiler. Air seals were ultimately adopted to minimize this problem. By about 1915 the possible use of waste heat boilers received almost universal attention in the cement industry which resulted in their installation in a number of kilns throughout the country. By 1936 approximately one-third of the 63 wet-process and one-half of the 50 dry-process kilns in the U.S. employed waste heat boilers.

During the 45 years since then, however, continuing technical problems as well as other contributing factors have resulted in the abandonment of most waste heat boiler systems in the cement industry. Four basic factors have been instrumental in this trend as pointed out in Reference 4-9:

- (1) Emphasis on power production -- not cement production.
- (2) Excessive boiler maintenance for fouling and corrosion.
- (3) Inexpensive energy costs.
- (4) Low cycle efficiency at lower temperature.

Today, there are apparently only four cement plants in the United States which generate electricity using waste heat exhausts:

1. National Gypsum Company  
Alpena, Michigan
2. Gifford-Hill Company  
Oro Grande, California
3. Medusa Cement Company  
Sylvania, Ohio
4. Lehigh Portland Cement Company  
Independence, Kansas.

With the exception of the Lehigh plant in Independence, Kansas, which uses gas as the primary fuel, all of these plants utilize coal as the primary fuel. Apparently, standard waste heat boiler equipment is utilized at each of these locations. For example, waste heat boilers were recently installed on two kilns at the Riverside Cement Company, Gifford-Hill Company at Oro Grande, California. The two parallel systems each utilized an economizer, boiler, and superheater with the boilers rated at 755 K and 4.83 MPa. Although there is considerable interest in the use of Organic Rankine Cycle (ORC) bottoming cycles in the cement industry, all of the waste heat boilers presently operating in this country use steam as the working fluid.

#### 4.4 CLINKER COOLERS

The clinker leaves the kiln at a temperature of about 1645 K. Ambient air is used to cool the clinker prior to grinding and mixing it with gypsum to produce cement. It has been found that rapid cooling of the clinker produces clinker which is both of superior quality and easier to grind, thus reducing the power requirements for the grinding process. Quickly cooled clinker results in cement with high glass content which in turn tends to suppress dusting of the clinker and also to strengthen the resulting cement. Rapid quenching of the clinker with air also minimizes the formation of large crystals of periclase ( $\text{MgO}$ ) which tend to produce cements with the undesirable characteristics of increasing in volume upon hydrating.

Additional considerations of this phenomenon, including a detailed consideration of the constituents and chemistry of the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system, may be found in Bogue (Reference 4-10).

In addition to stabilizing the clinker as described above, the use of a clinker cooler allows the recuperation of a portion of the energy from the hot clinker. Regardless of the type of fuel used, the volume of air required in the combustion process of rotary kilns contains approximately 10 percent primary air which is mixed with the fuel to ensure effective control of the flame conditions (Reference 4-11). The remaining air which is required in the combustion process, known as the secondary air, is supplied in the form of heated air from the clinker cooler. In general, clinker coolers may be classified in heat exchanger terminology as being of the crossflow or counterflow type. There are basically three types of clinker coolers -- the grate cooler, the planetary cooler, and the separate rotary cooler -- and these will be discussed briefly.

The grate cooler is of the crossflow type and, of the three types mentioned above, is by far the most widely used. Basically, the clinker forms a layer normally about 0.38 m thick which is transported along the grate. The cooling air is blown from below the grate by fans and thus cools the clinker by direct contact heat transfer between the clinker and the air. A portion of this air is used as secondary air in the kiln and the remaining vent air is cleaned in a dust collector and discharged to the atmosphere. In some cases the cleaned hot air is used to dry raw material or coal, to heat water, to preheat fuel oil, or to heat a building (Reference 4-12). Fines which seep through the grate are removed from the undergrate air chambers using either internal drag chain conveyers with air seals or through outlets in the cooler floor.

The planetary clinker cooler is of the counterflow type and consists of several tubes, usually 10 in number, which surround the kiln and which have a length-to-diameter ratio of about 10-to-1. The clinker and cooling air pass through the inside of the tubes, with lifters positioned and shaped according to the properties of the clinker, which rotate in a planetary manner. This



type of cooler is not as efficient in cooling the clinker as the grate type cooler. The rotary cooler is also of the counterflow type and is the oldest type of clinker cooler. It is usually located below the kiln and consists of a revolving cylinder following the rotary kiln. The normal length-to-diameter ratio is 10-to-1, with the slope ranging between four and seven percent, and the cooler rotates at a speed of 3 rpm.

The grate cooler is characterized by its excellent capacity for rapid cooling and is recommended when a low clinker exit temperature is required. Also, the supply of combustion air to the kiln when a separate precalciner is being used may be facilitated by the use of the grate cooler. In order to describe the function of the grate cooler in more detail, consider Table 4-1 in which the air distribution for the different types of kiln systems is given in tabular form. In all cases the clinker enters the cooler at 1645 K and leaves at 340 K. Basically, the portion of the heated air which is at the highest temperature is recuperated and used as secondary air in the kiln. The percentage of air used for this purpose ranges from 45 percent for the wet process to a low of 12 percent for the precalciner process. In the latter process, 18 percent of the recuperated air goes directly to the precalciner for combustion in the last stage of the preheater system. The remaining portion of the heated air which is generally referred to as the vented air, is at a much lower temperature as indicated in Table 4-1 and is generally discharged to the atmosphere after going through a baghouse where most of the particulate matter is removed. This stream ranges in temperature from 410 K for the wet process to 480 K for the preheater and precalciner processes, with 55 percent of the clinker cooler exhaust air vented in the wet process to 70 percent in the preheater and precalciner processes.

Table 4-1. Air Distribution in Grate Clinker Coolers for Different Type Kiln Systems\* (References 3-7 and 4-13)

Process	Recuperated Air					
	Air to Kiln		Air to Precalciner		Vented Air	
	Percent	Temperature K	Percent	Temperature K	Percent	Temperature K
Wet	45	935	---	---	55	410
Long-Dry	35	1035	---	---	65	445
Preheater	30	1145	---	---	70	480
Preheater/ Precalciner	12	1420	18	965	70	475
*Clinker enters clinker coolers at 1645 K and leaves at 340 K						

## SECTION 5

### GAS-SIDE FOULING MECHANISMS

The purpose of this section is to consider the basic mechanisms which may be involved in gas-side fouling. Very little work has been undertaken on gas-side fouling in cement plant applications. However, many related studies have been done in other areas such as the gas turbine, power, and nuclear industries, atmospheric environmental studies, and the design of gas-cleaning equipment. Information from these seemingly diverse fields will be drawn upon as appropriate, especially as it seems applicable for heat exchangers used in the cement industry. Following a classification of the various types of fouling, particulate fouling deposition mechanisms will be considered. Next, those mechanisms relating to corrosion, corrosion fouling, and chemical reaction fouling will be reviewed. Finally, a consideration of removal mechanisms and erosion will conclude this section. Gas-side fouling studies relating specifically to cement plant experience will be considered in Section 6.

#### 5.1 CLASSIFICATION OF FOULING

Fouling has been defined as the buildup of scale on a heat exchanger surface and includes the associated problems of corrosion and erosion. In general, the fouling layer has a relatively low thermal conductivity and therefore retards the flow of heat. In addition, the fouling layer reduces the flow area and hence increases the pressure drop. It has become popular to classify fouling into the following six categories (References 5-1 and 5-2):

- (1) Precipitation Fouling - the precipitation of dissolved substances onto the heat transfer surface. Where the dissolved substances have inverse rather than normal solubility versus temperature characteristics, the precipitation occurs on superheated rather than subcooled surfaces and the process is often referred to as scaling.

- (2) Particulate Fouling - the accumulation of finely divided solids suspended in the process fluid onto the heat transfer surface. In a minority of instances settling by gravity prevails, and the process may then be referred to as sedimentation fouling.
- (3) Chemical Reaction Fouling - deposits formed at the heat transfer surface by chemical reactions in which the surface material itself is not a reactant.
- (4) Corrosion Fouling - the heat transfer surface itself reacts to produce corrosion products which foul the surface and may promote the attachment of other foulants.
- (5) Biological Fouling - the attachment of macro-organisms (macro-fouling) and/or micro-organisms (micro-biofouling or microbial fouling) to a heat transfer surface, along with the adherent slimes often generated by the latter.
- (6) Solidification Fouling - freezing of a liquid or some of its higher melting constituents onto a subcooled heat transfer surface.

Of these six categories, particulate fouling, chemical reaction fouling, and corrosion fouling are of particular interest as far as gas-side fouling is concerned. These three types of fouling, and the role they play in gas-side fouling, will be considered in Sections 5-2 and 5-3. Two related phenomena -- erosion and corrosion -- in which the prime concern is the wearing away of the surface material, rather than the buildup of a layer on the surface, are also of interest here.

Erosion may be defined as a wearing away of a solid surface, in this case by the impact of particulate matter produced from both the feed and the ash in the fuel, coming into contact with the surface. Corrosion is the destruction of a metal or alloy by means of a chemical or electrochemical reaction with its environment, which may be either a liquid or a gas. In order to avoid confusion, the distinction between corrosion and corrosion fouling

needs to be emphasized. In corrosion fouling, the corrosion products from the heat transfer surface produces a fouling layer on the surface which retards the transfer of heat. On the other hand, corrosion results in a reduced amount of surface material as a consequence of a chemical reaction between the surface its environment.

## 5.2 PARTICULATE FOULING DEPOSITION MECHANISMS

A consideration of particulate fouling deposition mechanisms involves two basic phenomena: (1) transport of particles to the wall, and (2) attachment or adhesion of the particles to the surface. There are several different mechanisms by which particles may be transported to and deposited onto a surface, and the purpose of this section is to provide some pertinent details regarding these phenomena. However, before discussing some specific deposition models, the various forces which are important in particulate fouling will be mentioned briefly. Of course, in some cases the transport itself is due primarily to a given force, and in that case discussion will be deferred until that particular type of mechanism is considered in more detail.

### Particle Forces

Gravity is important in relatively static systems in which the particles are greater than  $1\text{ }\mu\text{m}$  in diameter. However, in the cement industry static systems are of little interest so gravity is not expected to be of any consequence in gas-side fouling in cement plants. Drag forces have contributions from both skin friction and form drag and tend to move particles along. For spherical particles the drag coefficient is a function of the Reynolds number and is well known for a single particle; however, for systems of particles the drag force is more difficult to predict because of the interaction among the particles. The inertia forces are proportional to the particle density, diameter, and relative velocity between the particle and the fluid. Thus, as the particles become more dense, the diameter becomes larger, or the particle velocity increases, inertia forces tend to become more significant. As a particle approaches a solid surface, a lift force known as the Magnus effect

is exerted on the particle and is the force which results by virtue of a rotating object in a shear flow. The particle must travel faster than the surrounding fluid moving parallel to the wall if the particle is to be directed toward the wall. Conversely, if the particle travels more slowly than the surrounding fluid parallel to the wall the particle will be directed away from the wall. Additional forces result from the phenomena of electrophoresis, thermophoresis, and diffusiophoresis, and these phenomena will also be discussed.

### Convective Mass Transfer

Convective heat transfer has been defined by Rohsenow and Choi (Reference 5-3) as conduction with fluid motion. In a similar way, convective mass transfer may be described as diffusion with fluid motion. For small particles at sufficiently low velocities, the particle mass transport will be by laminar, or Brownian, convective mass transfer. However, for particles greater than 1  $\mu\text{m}$ , Brownian motion will be negligible. If the bulk stream is moving under turbulent flow conditions, there will be a movement of turbulent eddies normal to the mainstream flow which can transport particles toward the wall. In general, then, the mass flux of particulate matter in a gas stream may be described by the relation

$$J = (D + \epsilon)dc/dy \quad (5-1)$$

where

$J$  = particle mass flux

$D$  = diffusion coefficient

$\epsilon$  = eddy diffusivity for turbulent mass transfer

$c$  = particle concentration

$y$  = coordinate normal to the surface

In the turbulent boundary layer,  $\epsilon$  will be much larger than  $D$  in the turbulent core, while in the laminar sublayer the opposite is true. However, recent work has shown that the "laminar" sublayer in many cases is not truly laminar, and this point will be considered in more detail later.

## Inertial Impaction

For particles larger than about  $1\text{ }\mu\text{m}$ , the inertial effects of particles in gases can become very important. For example, when a flow is turned, particle inertia can cause a particle to deviate from the flow streamlines. Particle deposition resulting from this type of process is known as inertial deposition, and this phenomenon can occur in either internal or external flows. Inertial impaction is often the controlling mechanism for the removal of larger particles in gas-cleaning devices such as filters, scrubbers, and cyclone separators. Inertial impaction can also be an important deposition mechanism in large utility gas turbines. Since cement dust particles can be as large as  $100\text{ }\mu\text{m}$ , it would be expected that in certain situations inertial impaction could be a very important deposition mechanism.

An additional problem is encountered as particles approach a surface under turbulent flow conditions. As discussed in the previous section, the eddy diffusivity is generally believed to be much smaller than the diffusion coefficient  $D$  in the laminar sublayer. For particles larger than about  $1\text{ }\mu\text{m}$ , however, the experimental rates of deposition based on this assumption are much larger than the values predicted by Eq. 5-1. In order to overcome this difficulty, Friedlander and Johnstone (Reference 5-4), proposed the concept of a "particle stopping distance" which they defined as the distance required to bring a spherical particle to rest in a stagnant fluid under the action of the Stokes drag force once it has been given an initial impetus. Thus, it was postulated that particles moving normal to a solid surface need to be carried to within one stopping distance of the wall, and they would then coast the remaining distance across the boundary layer under their own inertia. Turbulent eddies were assumed to carry the particles from the bulk stream to the point where they could coast to the wall. Further details on inertial deposition may be found in Friedlander (Reference 5-5).

## Thermophoresis

Thermophoresis is the movement of small particles in a fluid under the influence of a temperature gradient. Particles are bombarded by higher energy molecules on their "hot" side, and thus the particles tend to move toward a cold surface and away from a hot surface. Whitmore and Meisen (Reference 5-6) have shown that the thermophoretic velocity,  $V_t$ , is given by

$$V_t = \alpha \nu \nabla T / T \quad (5-2)$$

where the coefficient  $\alpha$  for gases is given by

$$\alpha = 1.8 / (k_p / k_g + 2) \quad (5-3)$$

where

$V_t$  = thermophoretic velocity

$\alpha$  = coefficient given by Eq. 5-3

$\nu$  = kinematic viscosity

$\nabla T$  = temperature gradient

$T$  = fluid temperature

$k_p$  = thermal conductivity of the particle

$k_g$  = thermal conductivity of the gas

Thermophoresis is important for particles below 5  $\mu\text{m}$  and becomes dominant at about 0.1  $\mu\text{m}$ . Depending on the magnitude of the temperature gradient, and the other parameters involved in Eq. 5-2, thermophoresis can be important in both laminar and turbulent flows. In particular, it has been determined that this phenomenon can be a significant factor in particle transport in fossil-fired boilers, flow inside tubes, and combustion turbine blade passages (References 5-7, 5-8, and 5-9).



## Electrophoresis

Electrophoresis may be defined as the deposition of particulate matter onto a solid surface due to electrostatic charges. In some instances, electrical forces can be very important in the transport of solid particles to a surface. In general, particles may collect charges by contact with a solid surface or with each other, from atmospheric electricity, from an ionized gas, or by emission. In cement kilns with suspension preheaters, the preheaters are ideal sources of particle charging since the particles tend to come in contact not only with each other but also with the surface of the cyclone separators. The most important surface forces are the London-van der Waals forces which are always attractive. The electrical double layer interaction forces are attractive if the particle and wall have zeta potentials of opposite sign and repulsive if these charges are of the same sign. Soo (Reference 5-10) has shown that electrostatic deposition will always occur when

$$\emptyset \rho_p^2 d_p^2 R^2 (q/m_p)^2 / 18 \epsilon_0 D \mu > 8 \quad (5-4)$$

where

$\emptyset$  = volume fraction solid

$\rho_p$  = density of the particle

$q$  = electrical charge

$m_p$  = mass of the particle

$R$  = gas constant

$\epsilon_0$  = permittivity in free space

$D$  = diffusion coefficient

$\mu$  = gas viscosity

The magnitude of  $q/m_p$  depends on the materials, both particles and conveying pipe, as well as the handling. Charging by surface contact gives a  $q/m_p$  of magnitude  $10^{-3}$  to  $10^{-5}$  C/kg. In general, the smaller a particle in a suspension, the more significant the effect of the electrical charge it carries. Electrical forces become increasingly important on

charged surfaces as particle size decreases below about 0.1  $\mu\text{m}$ . For larger particles, very strong electrical fields are required to influence deposition. In some cases where electrophoresis is a problem, it can be overcome by grounding the heat transfer surface.

### Diffusiophoresis

When vapor condenses onto a surface, a diffusiophoretic force is exerted on particles in the direction toward the surface. This force has two sources: (1) the net flow of molecules to the droplet, a "wind" of sorts called the Stefan flow, and (2) a component due to the vapor concentration gradient and the difference between the molecular weight of the vapor and the molecular weight of air (Reference 5-11). When vapor condenses onto particles, there is another important effect, i.e., the particles become larger and therefore are more easily captured by settling or by inertial impaction. These effects can be important for submicron particles. Regarding diffusiophoresis, condensation will enhance collection and evaporation will impede collection. It is not known how important this phenomenon may be for gas-side fouling in cement plants.

### Particulate Fouling Deposition Models

Several deposition models have been proposed for particulate fouling and the most important of these will be considered in this section. Ultimately, deposition models must consider transport to the wall, particle-particle and particle-surface interactions, and the probability that not all of the particles which reach the surface actually stick to the surface. Although some work has been done in this latter area, it is still not known precisely why some particles stick and others do not.

One deposition model which has received considerable attention is the turbulent burst model of Cleaver and Yates (Reference 5-12). Recent experimental studies have shown that the viscous sublayer in the turbulent boundary layer is not truly steady. Fluid is being continually swept toward

the wall, a phenomenon which Cleaver and Yates have referred to as "downsweeps", and ejected away from the surface by turbulent "bursts". They proposed a model for the deposition rate assuming that particles are convected to the wall by this downsweep action. Their model predicts deposition ranging from diffusion controlled situations through inertia controlled situations, obtained by considering these contributions to be additive, and shows satisfactory agreement with existing experimental data. The point of minimum deposition is identified by the condition

$$Re_p Sc^{1/3} = 1.11 \quad (5-5)$$

where

$Re_p$  = the particle Reynolds number

$Sc$  = the Schmidt number

As the  $Re_p Sc^{1/3}$  product becomes larger than 1.11 the deposition rate decreases, and as this product becomes smaller than 1.11 the deposition rate increases.

Cleaver and Yates (Reference 5-13) refined their model to take into account the fact that re-entrainment can affect the rate of deposition. In other words, they assumed that between turbulent bursts from the surface, particles were being continuously deposited by the downsweeps. They found that the wall shear stress is the controlling parameter in such situations. Below a critical value of  $\tau_w$ , for which removal can occur, deposition varies linearly with time, but above this critical value the deposition rate depends on the choice of the time interval over which the measurements are made. The dependence of deposition on the wall shear stress for combined deposition and removal has been formulated for the cases where diffusional, inertial, and gravitational forces are dominant. Comparison with data from the literature confirms this general trend, but additional work must be done to refine this model.

The actual adhesion of a particle to a surface depends on the London or van der Waals interaction and is influenced by the physical parameters of the

system. In general, particle and surface materials, particle size, and surface roughness are some of the important parameters. Particle and surface temperatures are also important parameters, but little is known about their effect. The van der Waals and electrostatic forces are the most important factors in particle adhesion. The electrostatic forces may be of comparable magnitude to or greatly exceed the van der Waals forces, depending upon the parameters given in Eq. 5-4.

In considering the deposition of particles onto a surface, the concept of a sticking probability may be introduced to account for the fraction of particles which stick to the surface, irrespective of how they arrive at the surface. Beal (Reference 5-14) defined the sticking probability to be

$$p = k_t x / [k + V_{pn}(1 - x)] \quad (5-6)$$

where

$k_t$  = the transport coefficient of the particles near the surface

$x$  = the ratio of the observed deposition coefficient to predicted deposition coefficient with  $p = 1$

$V_{pn}$  = the particle velocity normal to the surface

A more fundamental approach to the sticking probability, based on fluid mechanics and chemical-kinetic arguments, was proposed in the fouling model of Watkinson and Epstein (Reference 5-15). They assumed adhesive forces to be physico-chemical in nature and to follow an Arrhenius relationship with temperature, while the removal forces were taken to be proportional to the wall shear stress and therefore to the  $f V^2$  product where  $f$  is the friction factor and  $V$  is the bulk fluid velocity. Since  $p$  is directly proportional to the adhesive forces and inversely proportional to removal forces

$$p = A_0 e^{-E/RT} / f V^2 \quad (5-7)$$

where

$A_0$  = a constant

$E$  = activation energy

Epstein (Reference 5-1) has interpreted the constant  $A_0$  in terms of the minimum friction velocity which will inhibit the deposition of particles in the first place. The phenomena of adhesion of particles is influenced by many factors. As the fluid velocity increases, the sticking probability decreases rapidly and as the particle diameter increases the sticking probability decreases. Also the force of adhesion of particles on a clean surface, or on a surface with a layer of deposited particles, influences deposition of additional particles.

Beal has carried out several studies dealing with particulate fouling deposition models, and his major contributions will be reviewed here briefly. In a classical study, Beal (Reference 5-16) proposed a model for predicting the deposition of particles entrained in a turbulent flow. His model was obtained by integrating Eq. 5-1, taking the Brownian or laminar diffusion, turbulent diffusion, and inertial effects into consideration. Thus, his model was formulated so as to be valid for particles ranging in size from very small diameter to moderately large particles, i.e., from molecular size to  $100\text{ }\mu\text{m}$  in

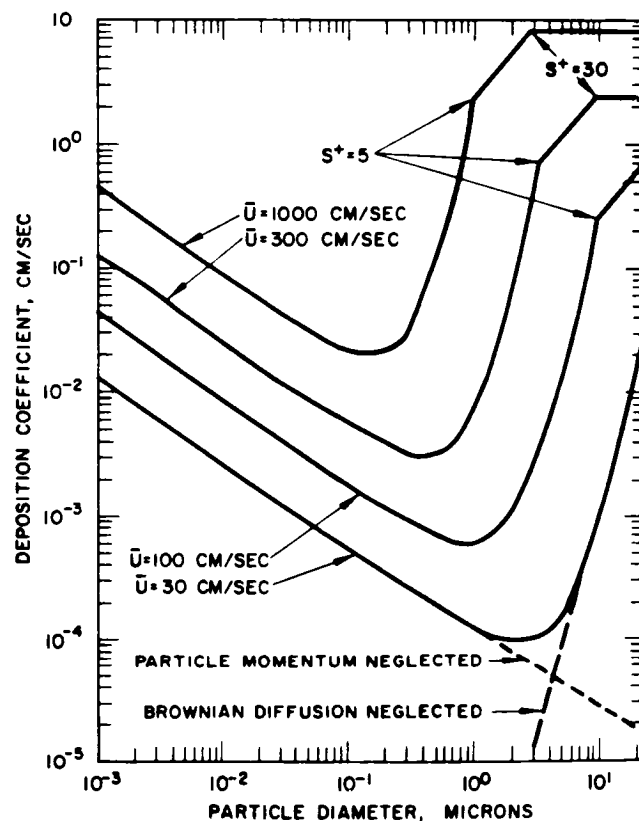


Figure 5-1. Effect of Particle Size and Velocity on Deposition According to Beal's Model (Reference 5-16)

diameter. At small diameters molecular diffusion is controlling and at large diameters the deposition is momentum controlled as shown in Figure 5-1. The proposed model was compared with experimental data for particles ranging in diameter from  $10^{-3}$   $\mu\text{m}$  to 30  $\mu\text{m}$  and velocities between 0.30 m/s and 61.0 m/s. Good agreement with the experimental data was considered justification of the model. In all cases the sticking probability was taken as being 1.0, i.e., all the particles reaching the surface were assumed to stick to the surface. In a later paper (Reference 5-14), based on an analysis of experimental particle deposition data from the literature, Beal formulated a correlation for the sticking probability in terms of the dimensionless stopping distance,  $S^+$ . For particles in air the sticking probability is 1 for small values of  $S^+$  and inversely proportional to  $(S^+)^3$  for  $S^+ > 4.5$ . In yet another study Beal (Reference 5-17) developed a method for predicting agglomeration rates in turbulent flow of suspensions. Whenever large numbers of particles are present in a gas, they tend to collide with one another. If upon collision the particles stick together the process is termed agglomeration or coagulation. In a typical situation, the agglomeration rate exceeds the deposition rate for particles smaller than 0.01  $\mu\text{m}$ , but the reverse is true for particles larger than 10  $\mu\text{m}$ . In the intermediate range of 0.1 to 1.0  $\mu\text{m}$ , the rates are about equal.

Several other deposition models have been formulated but have not been as widely accepted as those discussed here. These studies include those of Rouhiainen and Stachiewicz (Reference 5-18) who calculated particle trajectories under the combined action of the Stokes drag force and a shear-induced lift force. Sehmel (Reference 5-19) formulated a deposition model taking into consideration turbulent diffusion, Brownian diffusion, and gravity settling. His model predicted deposition for particle sizes of  $10^{-3}$  to  $10^2$   $\mu\text{m}$  and particle densities of 1 and 10 gm/cm<sup>3</sup>.

### 5.3 CORROSION, CORROSION FOULING, AND CHEMICAL REACTION FOULING MECHANISMS

The mechanisms related to corrosion, corrosion fouling, and chemical reaction fouling are considered in this section. Since these phenomena are so closely related, it seemed somewhat artificial to try and separate them; hence, they have been grouped together under the same heading for discussion purposes.

Since most of the present day cement kilns in the U.S. are using pulverized coal as the fuel, with a continuing trend in this direction, only those fouling and corrosion mechanisms associated with coal as a fuel will be considered here. Most of the information in this section has been taken from the coal-fired boiler related literature.

### Background Information

A knowledge of the various minerals found in coal is important in trying to understand the various chemical reaction fouling and corrosion mechanisms. Minerals in coal occur primarily in four major groups: shale, clay, sulfur, and carbonates. The ash is composed primarily of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{Fe}_2\text{O}_3$  with trace amounts of  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{SO}_3$ , and  $\text{Cl}$ . (References 5-20 and 5-21). The specific combination of these elements varies by coal rank and also depends on the metamorphosis of the coal. The presence of the various impurities in the coal, along with the ash chemistry, will be important factors in those fouling and corrosion mechanisms related to chemical reaction transformations.

In general, superheater deposits are formed as a result of the interaction of dry flyash with condensable material usually appearing as inherent material in the coal. Sodium and potassium generally volatilize in the furnace and then condense out in the form of alkalis and sulfates. Alkalies released from low sulfur coals tend to condense on the flyash, forming sticky aluminosilicates which create sintered deposits in the convection portion of the boiler. Alkalies released from high sulfur coal, on the other hand, tend to form complex aluminum or iron alkali sulfates with relatively low melting temperatures. It is clear that the distribution of impurities in the coal and the ash chemistry of the coal are both important parameters in chemical reaction related fouling and corrosion mechanisms. Some specific details will now be examined.

## Alkali-Metal Deposition and Corrosion

One of the most important chemical reaction fouling mechanisms is that resulting from alkali-metal sulfates. The presence of sulfur trioxide is a key element in this fouling process which is generally believed to proceed as follows (References 5-22, 5-23, and 5-24):

- (1) Sodium and potassium are volatilized in part from the mineral matter in the high-temperature flame forming  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ .
- (2) During combustion, pyrites are dissociated thermally and, with the organic sulfur in the coal, react with oxygen, forming mostly  $\text{SO}_2$  and some  $\text{SO}_3$ .
- (3) As the result of normal oxidation between 590 and 700 K, a thin layer of oxide forms on the metal surface. The rate at which this oxide layer grows decreases as the thickness increases, and a more-or-less limited thickness is approached.
- (4) The  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  then react with  $\text{SO}_3$ , either in the gas stream or on the tube surface, to form sodium or potassium sulfate,  $\text{Na}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$ , according to the reactions



These low-melting materials attract other particulates, eventually building up a moderately thick deposit. During this process,  $\text{SO}_3$  is evolved as the result of reactions in the ash during the melting process.

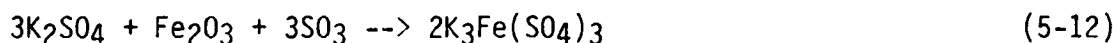
- (5) The alkali sulfates, iron oxide, and  $\text{SO}_3$  then react to form the complex sulfates,  $\text{Na}_3\text{Fe}(\text{SO}_4)_3$  or  $\text{K}_3\text{Fe}(\text{SO}_4)_3$ , which are molten at about 865 K in a high- $\text{SO}_3$  environment ( ~1000 ppm).



The availability of  $\text{SO}_3$  is an important part of this mechanism. The presence of iron oxide is necessary for the catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  according to the reaction



Concentrations of 0.11 percent sulfur trioxide are required prior to the conversion of solid  $\text{K}_2\text{SO}_4$  into liquid  $\text{K}_2\text{S}_2\text{O}_7$  at 755 K, while at 700 K only 200 ppm  $\text{SO}_3$  are necessary (Reference 5-25). Similarly, the possible reaction of the alkali sulfates with iron sulfate was demonstrated by Corey et al. (Reference 5-23) to occur only when the  $\text{SO}_3$  concentrations were greater than 250 ppm



Similar reactions may be written for sodium by replacing K with Na in Eqs. 5-11 and 5-12. Several researchers, including Clark and Childs (Reference 5-26), have pointed out the desirability of low excess air. The most generally accepted explanation for the beneficial effect of low excess air is that there is less free oxygen available for the transformation of  $\text{SO}_2$  to  $\text{SO}_3$  according to Eq. 5-10. Thus, reducing the amount of excess air will reduce the amount of  $\text{SO}_3$  and under conditions when the concentration of  $\text{SO}_3$  is less than about 0.02 percent, corrosion will not occur to any appreciable extent -- even in the presence of alkali sulfates (Reference 5-23). Also, corrosion will not occur in the absence of alkali-metal sulfates.

Alkaline earths can inhibit the formation of either potassium or sodium iron trisulfate which may be produced by either of the reactions given in Eqs. 5-11 and 5-12. Calcium and magnesium are known to have an inhibiting effect on the formation of potassium or sodium iron trisulfates by the formation of more stable compounds. When sufficient concentrations of either  $\text{CaO}$  or  $\text{MgO}$  are present, in either the coal ash or after calcination of the sorbent material,

reaction with gaseous sulfur trioxide will produce calcium or magnesium sulfate according to the reactions



These sulfates can, in turn, react with the alkali sulfates formed by Eqs. 5-8 and 5-9 to form an alkali calcium (or magnesium) trisulfate complex by the reactions



Reactions similar to Eqs. 5-15 and 5-16 may be written for sodium by replacing the symbol K in these equations by Na. The resulting calcium (or magnesium) trisulfate is less corrosive than the alkali iron trisulfate phases. Field experience, as well as that in a laboratory furnace, has also shown that most coals treated with sufficient lime (CaO) to control the sulfur oxides produce a softer, more friable deposit which is easier to control with soot blowers. The calcium compounds produce a less dense, more bulky deposit than the equivalent iron salt; therefore, the deposit is less tenacious and easier to remove. Another possibility for reducing the fouling-corrosion potential is by reducing the active alkali content of the coal, i.e., Na<sub>2</sub>O and K<sub>2</sub>O.

Tufte and Beckering (Reference 5-27) investigated the mechanism of chemical reaction fouling in lignite and found a similar phenomena as described above in that sodium sulfate was deposited on the tubes. They speculated that the basic deposition of Na<sub>2</sub>SO<sub>4</sub> was due to vapor condensation, particle diffusion, and eddy diffusion. The deposition of the flyash particles was believed to be due to inertial impaction of the larger than average flyash particles about the tube stagnation point. This argument has been proposed by several investigators and substantiates the fact that the largest deposits appear on the upstream side of the tube in the vicinity of the stagnation point as shown in Figure 5-2.

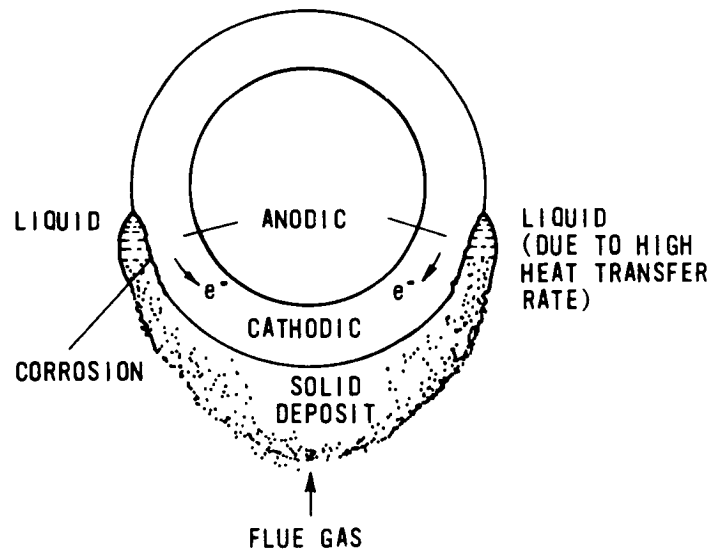


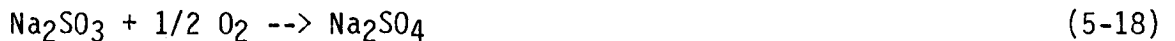
Figure 5-2. Schematic Illustration of Gas-Side Fouling Deposit and Corrosion on Boiler Tube (Reference 5-7)

Tufte and Beckering also pointed out that  $\text{Na}_2\text{SO}_4$  will be formed from  $\text{SO}_3$  in high sulfur streams and  $\text{Na}_2\text{CO}_3$  in low sulfur streams. They suggested that either species will act to flux deposits, but the sodium carbonate deposition mechanism has not been investigated nearly to the extent which  $\text{Na}_2\text{SO}_4$  has. They suggested two possible ways to mitigate the sodium sulfate type of fouling: (1) use an additive to tie up sodium in a non-reactive form to inhibit its fluxing action, and (2) use an additive sprayed directly on the pulverized coal that would eventually enter the ash and raise its fusion temperature or otherwise inhibit the sodium fluxing action.

Hein (Reference 5-28) has carried out a preliminary study of gas-side fouling in a coal-fired situation. Although not specifically related to alkali-metal deposition and corrosion it is nevertheless of interest here. He found that the deposition mechanisms can be influenced by excess air level, burner-dependent mixing between fuel and combustion air, particle size distribution of the coal, and combustion air temperature. Further research is underway to quantify the effects of these parameters.

## The Mechanism of Sodium Sulfate Deposition

Brown (Reference 5-29) experimentally studied the rate of deposition of sodium sulfate from combustion gases produced by burning a liquid fuel (sodium naphthenate and carbon disulfide added to kerosene) in a pilot-scale furnace. Deposits were produced on the outside of circular-tube stainless steel specimens exposed to the combustion gases at surface temperatures of 695 K to 1015 K for periods up to 10 hours. Under conditions of low excess air, which would generally be the case in cement kilns, sodium sulfate is formed by the chemical reactions



Brown proposed the following explanation for the deposition of  $\text{Na}_2\text{SO}_4$  onto the tube surface based on his study. The theoretical sodium sulfate dew-point temperature for a gas stream carrying 53 ppm  $\text{Na}_2\text{SO}_4$  (his test conditions) is 1143 K. Thus, if the combustion gases are exposed to a surface below the dew-point temperature, the vapor condenses within the dew-point isotherm which is located at some distance from the tube surface. The condensed droplets are then transported toward the tube surface under the influence of thermal forces. (Since the particles were believed to be about  $0.1 \mu\text{m}$  in diameter, the thermal forces would undoubtedly be due to thermophoresis). If the tube temperature is sufficiently low, the droplets will solidify before reaching the surface and are not likely to become attached to the surface. However, as the tube temperature increases and approaches the dew-point temperature, the deposition process will become dominated by vapor diffusion and the deposition rate will increase. Simultaneously, at temperatures near the dew-point temperature, the vapor diffusion rate tends to decrease. Thus, as a consequence of these opposing trends, the deposition rate will pass through a maximum at a temperature near, but somewhat below, the dew-point temperature. Thus, at surface temperatures less than about 673 K (400C) and greater than 1073 K (800C), no deposition was

observed in his experiments as shown in Figure 5-3. Between these temperature levels,  $\text{Na}_2\text{SO}_4$  was deposited on the tube surface with a maximum rate of deposition in the vicinity of 875 K to 975 K. Although his study indicated a  $\text{Na}_2\text{SO}_4$  dew-point temperature of about 1073 K, this dew-point temperature in general will vary depending on the concentration of the sodium

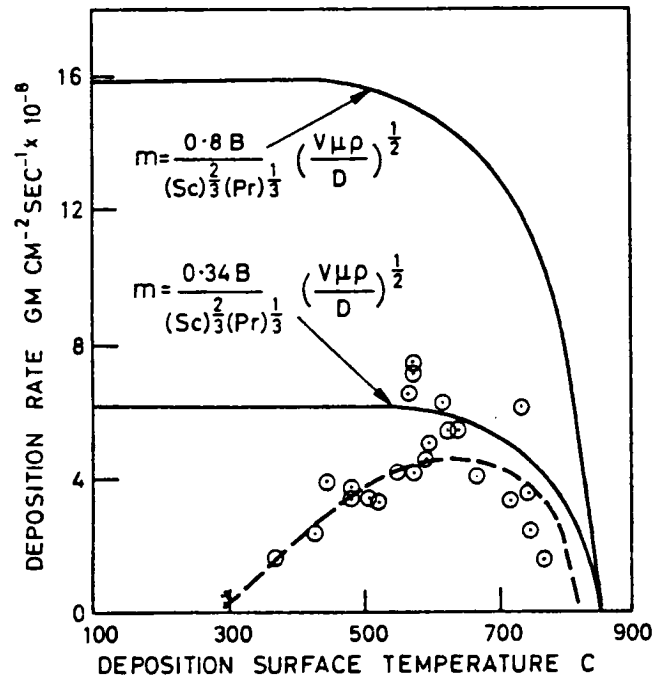


Figure 5-3. The Deposition Rate of Sodium Sulfate at 1.0 Percent Excess Air (Reference 5-29)

sulfate in the gas stream. Interestingly, he also found that while the chemical reactions producing  $\text{Na}_2\text{SO}_4$  are strongly dependent upon the amount of excess air in the gas stream, the rate of deposition of  $\text{Na}_2\text{SO}_4$  onto a cooled surface is only weakly dependent upon the amount of excess air used in the combustion process.

## Additional Corrosion Considerations

The interaction of corrosion and alkali-sulfate deposition mechanisms has been treated in an earlier portion of this section. Some additional considerations relating to corrosion will now be presented. Specific topics to be considered include corrosion from fuel ash, acid dew-point condensation, and hot corrosion mechanisms.

Neal and Northover (Reference 5-30) have summarized some of the most important conclusions relating to the corrosive aspects of fuel ash in fireside tube corrosion applications:

- (1) The rate of corrosion of boiler materials is very dependent on temperature.
- (2) Corrosion is greatly accelerated when surface temperatures are sufficiently high that immediately adjacent ash deposits are molten.
- (3) Corrosion is unlikely to be significant at surface temperatures below 875 K.
- (4) Typical high strength, oxidation resistant alloys have shown good high temperature corrosion resistance to some fuel ash samples and poor resistance to others.

Initial deposits on tube surfaces tend to be dry, porous, and friable, but as the deposit thickens, the surface temperature will increase rapidly and the outer layers will become sticky and hence attract particulates in the flow.

In a high sulfur environment, sulfur trioxide readily reacts with water vapor to form sulfuric acid according to the reaction



At the cold end of the boiler, the  $\text{H}_2\text{SO}_4$  can then condense on the metal surfaces and cause severe corrosion problems. The wet wall can also attract particulates and cause plugging and fouling of the heat transfer surface. Again, in addition to reducing the  $\text{H}_2\text{O}$  in the gases, the reduction of excess air to prevent the formation of sulfur trioxide according to Eq. 5-10 is a very important consideration. Although various surface coatings have been proposed to overcome the acid dew-point condensation problem, the present state-of-the-art is just to avoid the problem by making sure that the exit gas temperature remains a safe distance above the dew-point. Usually, this means that the outlet gas temperature should be no less than about 450 K to 425 K. There is also the possibility of the formation of hydrochloric acid,  $\text{HCl}$ , in situations where there is sufficient chlorine present in the exhaust gases.

Extensive efforts are being conducted at Westinghouse (Reference 5-25) to predict the composition of resulting gaseous and condensable combustion products in fluidized bed combustion systems. The formation of a liquid phase in the deposit is usually necessary for corrosion to occur at an appreciable rate as discussed in the preceding paragraph. Although a generalized hot corrosion mechanism has not yet been delineated, it appears that one or more of the following detrimental effects may be occurring simultaneously:

- (1) Removal of protective oxides on the metal surface through chemical reaction of corrodants formed within an overlying deposit.
- (2) Reactions of the protective scale with constituents in the flue gas and the overlying deposit.
- (3) Direct attack of the metal surface.

#### MgO Additives

The beneficial effects of  $\text{CaO}$  and  $\text{MgO}$  in mitigating gas-side fouling were briefly considered earlier in this section. The purpose of the present section is to consider in greater detail the important role which magnesium oxide plays in this process. Of all the possible additives,  $\text{MgO}$  has probably received the

greatest attention to date as a possible compound to minimize the effects of gas-side fouling in heat recovery applications.

In the early 1960s magnesium oxide, MgO, was used successfully to minimize gas-side fouling in coal-fired boilers. However, the dosages at that time required 0.4 to 3.0 percent of the fuel burned which were not economical. However, Radway and Boyce (Reference 5-31) have recently reported very positive gas-side fouling reductions at very low MgO treatment rates of 0.015 percent or less. In one phase of the study, treatment rates from 150 to 1250 ppm of MgO were utilized with a temperature-controlled deposition probe at 773 - 883 K to simulate conditions found in modern utility boilers. The deposits formed on the probe were friable, more powdery, and more easily removed when dispersed MgO was being used. In a second phase of the study the sulfuric acid deposition rate at 386 K surface temperature showed the reduction in acid deposition rate to be directly proportional to the MgO treatment level. Deposit analysis, X-ray diffraction, and differential thermal analysis were used to analyze the results. Although the basic mechanisms were not established with certainty, it is believed that the gas-phase reaction between MgO and SO<sub>3</sub> results in the formation of MgSO<sub>4</sub> according to the reaction



which is a very stable compound resulting in dry and very friable deposits. In addition, the reaction of sulfur trioxide with the magnesium oxide would leave less SO<sub>3</sub> to react with water to form sulfuric acid



The reduced formation of H<sub>2</sub>SO<sub>4</sub> with increasing MgO would thus explain the reduction in acid deposition with increasing MgO. Two key features of the tests were:

- (1) Extremely small MgO particle size. (The finer the size, the greater the surface area of MgO particles per unit mass).
- (2) Separate injection of the MgO and fuel so that the chemical loss of MgO with the bottom ash is minimized.



It is interesting to note that MgO is a naturally occurring constituent in the feed material in cement kilns. Thus, it is possible that in those situations where sufficient quantities of MgO are present in the raw materials, a naturally occurring additive is present in the feed.

#### 5.4 REMOVAL MECHANISMS AND MODELS

Many terms have been used to describe the removal process including re-entrainment, detachment, sloughing off, release, scouring, spalling, and erosion. Although all of these terms have been used in the literature, the terminology removal and re-entrainment will be used here to describe the natural movement of a portion of the fouled layer from the heat transfer surface, i.e., natural in the absence of external forces such as those produced by soot blowers. The purpose of this section is to review the mechanics of the removal process in gas-side fouling, and to consider briefly some of the removal models which have been proposed. Removal phenomena have not been studied as extensively as deposition mechanisms; consequently, the removal process is not as well understood as that of deposition.

Kern and Seaton (Reference 5-32) postulated that the time rate of change of the fouling resistance should be of the form

$$dR_f/dt = \Phi_d - \Phi_r \quad (5-22)$$

where

$\Phi_d$  = the deposition rate

$\Phi_r$  = the removal rate

$R_f$  = fouling resistance

$t$  = time

Furthermore, Kern and Seaton were apparently the first to recognize the importance of the shear stress in the removal process. They assumed  $\Phi_d$  to be a constant,  $\Phi_r$  to be proportional to  $R_f$ , and then integrated Eq. 5-22 to obtain

$$R_f = R_f^*[1 - e^{-At}] \quad (5-23)$$

where

$R_f^*$  = asymptotic fouling resistance

$A$  = a constant

A plot of Eq. 5-23 is shown in Figure 5-4 and indicates that the fouling resistance  $R_f$  asymptotically approaches the value  $R_f^*$  as  $t$  approaches infinity. However, in many practical situations the behavior shown in Figure 5-4 is not achieved because the assumptions underlying the derivation of Eq. 5-22 are not satisfied.

Taborek et al. (References 5-33 and 5-34) extended the work of Kern and Seaton and suggested that the removal function  $\Phi_r$  should be

$$\Phi_r = B_o \tau_w R_f / \Psi \quad (5-24)$$

where

$B_o$  = a constant

$\Psi$  = deposit strength

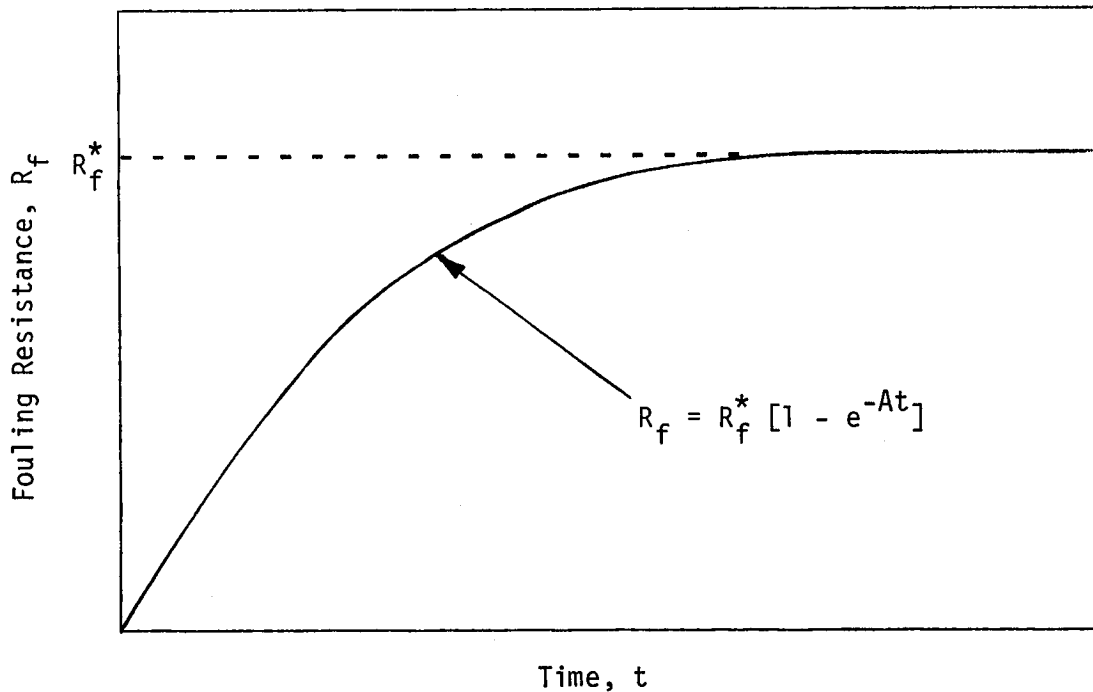


Figure 5-4. The Kern-Seaton Fouling Model Illustrating the Asymptotic Fouling Resistance Behavior (Reference 5-32)

Thus, they indicated that the removal function should be directly proportional to the wall shear stress and the fouling resistance and inversely proportional to the deposit strength. Since the friction factor may be interpreted as the dimensionless shear stress, the removal function may be alternatively interpreted as being directly proportional to the friction factor and the square of fluid velocity. Although the deposit begins to age as soon as it has been deposited on the surface, removal of the deposit may or may not begin as soon as deposition has been initiated. The scale strength  $\psi$  in the Taborek et al. model is a measure of the resistance of the deposit to removal or re-entrainment. The aging process may include changes in the chemical structure of the deposit, and it may also be affected by the surface temperature in some applications. Although there are exceptions, the deposit in general becomes more tenacious with time and hence becomes more difficult to remove, either by natural re-entrainment or by external techniques such as soot blowers. For example, deposits can sometimes be removed by heating the surface to a sufficiently high temperature such that the deposit strength is weakened to the extent that the fluid shear forces are adequate to remove the deposit. Since the removal process is directly proportional to the friction factor, it would appear that rough deposits would have a greater removal tendency than smooth deposits. In any case, experimental work has clearly shown that re-entrainment will not occur under laminar flow conditions. In other words, in order to have removal of the fouled layer, the mainstream flow must be turbulent.

Several experimental studies have shown that the laminar sublayer in the turbulent boundary layer is not truly laminar but, in fact, is unsteady and is continually disrupted by what Cleaver and Yates (Reference 5-35) have termed "turbulent bursts." These bursts are like miniature tornadoes and can cause instantaneous lift forces which are large enough to detach particles which have been deposited onto a surface. Cleaver and Yates have proposed the following criterion as a condition for re-entrainment

$$\tau_w d_p \geq \text{constant} \quad (5-25)$$

Although the mechanism of removal is not clearly established in their paper, this criterion does show general agreement with previous experimental studies. However, since their model does not include any reference to deposit strength, it is clear that Eq. 5-25 has limited applicability.

A final type of removal mechanism which may be of importance in cement plant applications is known as "splashing." Bagnold (Reference 5-36) observed splashing of particles when a traveling particle impacted a non-sticking layer of previously deposited particles. Seman and Penny (Reference 5-37) noted that particles striking a layer of electrostatically deposited dust caused splashing and re-entrainment. Splashing is produced mainly by particles larger than those in the deposited layer. In general, it would be expected that the momentum of the impacting particles, i.e., both the mass and the velocity, would be an important parameter in removal by a splashing type mechanism. As part of a study concerned primarily with sticking probability, Beal considered the erosion of previously deposited particles (Reference 5-14). Based on two previously published sets of data, he found the erosion coefficient to be proportional to the drag force raised to the 0.88 power.

## 5.5 EROSION

Erosion can be a serious problem in particulate-laden flows and depends on the size distribution of the particles, the surface material, the temperature of the solid surface, the velocity of the particles, the velocity of the fluid, the properties of the particles, and the geometry involved. Hansen et al. (Reference 5-38) have reviewed the importance of various erosion parameters. The impingement angle for maximum erosion of ductile materials such as the commonly used steels ranges from about 20° to 45° with most investigators indicating 30° as a representative value. Erosion increases with both the particle velocity and particle size. At low concentrations, such as would be found in cement plants, erosion increases with particle flux. Interestingly, at high concentrations the effects of erosion tend to decrease because the particles impact each other. Sharp particles produce more erosion than smooth ones, but particle hardness -- provided the particles are harder than the surface material -- apparently has little or no effect. Finally, Hansen et al. have indicated that there are no material properties which can reliably correlate erosion resistance.

Kotwal and Tabakoff (Reference 5-39) in a recent study found that erosion due to fly ash is caused primarily by silica and alumina,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , both of which are present in cement kiln dusts. In coal-fired kilns, these particulates come from the ash in the fuel as well as from the feed itself. Kotwal and Tabakoff used 304 stainless steel and found that erosion: (1) is a maximum at an impingement angle of about  $30^\circ$ , (2) increases with both particle velocity and diameter, and (3) increases as surface temperature increases. The fly ash used in their tests had particulates which ranged in diameter from  $1\text{ }\mu\text{m}$  to  $100\text{ }\mu\text{m}$ , which essentially is the same range encountered in cement kiln and clinker dusts. Soo (Reference 5-10) has reported that erosion decreases as the gas pressure increases, but this observation is of little importance in cement plant applications where gas pressures are only slightly above atmospheric. In cement plant applications, the greatest potential for erosion occurs in the clinker cooler exhausts where the gases tend to be highly abrasive because of the particulates from the clinker.



## SECTION 6

### GAS-SIDE FOULING EXPERIENCE IN CEMENT PLANTS

Heat-transfer equipment used in the cement industry was described in Section 4. Gas-side fouling mechanisms, as they are believed to relate to the cement industry, were discussed in Section 5. Gas-side fouling experience in cement plants is documented in this section. The specific types of heat exchangers considered are the same as in Section 4 with the exception of clinker coolers which, because of their design and function, are not subject to gas-side fouling. Gas-side fouling mechanisms of interest here include particulate, chemical reaction, and corrosion fouling along with the related topics of corrosion and erosion.

#### 6.1 PREHEATERS

Reference 3-8 is an excellent paper dealing with field and laboratory experience with buildups in cement plants. Buildup is defined as an undesirable coating or accretion that can form in a kiln, preheater, or other parts of a kiln system. Thus, in contrast to fouling, buildups can occur on other than heat transfer surfaces. However, much of the information in this very important paper is of interest here, especially that relating to preheaters. Since such buildups occur on the surfaces of the cyclone separators, and not on heat-transfer surfaces per se, it might be argued that such deposits do not constitute fouling in the sense in which it is defined in this report. However, such buildups on suspension preheater surfaces can and do affect the direct contact heat transfer processes within the preheater.

In addition, the alkali sulfates and chlorides from the hot exhaust gases can condense directly onto the cool raw feed particulates in the preheater. This process increases the level of contaminants in the kiln gases, which in turn can contribute to gas-side fouling problems elsewhere in the system. Therefore, for these reasons buildups in preheaters will be given appropriate consideration here. In four-stage preheaters the tendency for buildups is least in the first stage and the greatest in the fourth or

bottom stage. In other words, the tendency for the formation of buildups increases with increasing temperature.

Data from the field and results from laboratory experiments at the Portland Cement Association are reported in Reference 3-8. Based on these studies, there are at least three basic chemical reaction mechanisms which contribute to buildup formation in preheaters (as well as elsewhere in the system):

- (1) The recarbonation of CaO in situ.
- (2) The formation of stable intermediate compounds such as spurrite,  $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$ , which are frequently catalyzed by trace components such as alkali chlorides.
- (3) Deposits which are formed due to the condensation of molten salts, especially alkali sulfates and chlorides, onto solid surfaces.

The recarbonation of CaO in situ may be explained as follows. If kiln dust that contains chloride and sulfate compounds comes into contact with surfaces made of steel, the chlorides will attack the steel to form  $\text{FeCl}_3$  (iron chloride) on the metal surface. Since iron chloride has a melting point of only about 535 K, it can act as a bonding agent causing particles of kiln dust -- primarily CaO,  $\text{SiO}_2$ , and clay -- to stick to the surface. Once the material has deposited, CaO (free lime) recarbonates in situ, i.e., on the surface, according to the reaction



to give the deposit both hardness and strength. Laboratory investigations and field experience both indicate that if the amount of chloride in the raw feed exceeds 0.015 percent, and if the plant is recycling all its dust without using a bypass, then chloride levels exceeding 1.0 percent can occur in the feed at the fourth-stage cyclone and at the riser duct. Many preheater buildups result at least in part from such excessive chloride concentrations in the system.



Chemical analyses from fourth-stage buildups in two different plants, designated as Plants A and B, were carried out. Both plants were using a raw feed containing  $0.045 \pm 0.005$  percent chloride and  $0.050 \pm 0.010$  percent fluoride. All of the kiln dust was returned with the feed in both plants. The analyses indicated that the fourth-stage buildup in Plant A consisted primarily of the compounds KCl, spurrite, and NaCl, with smaller quantities of  $\text{CaCO}_3$ ,  $\text{C}_{12}\text{A}_7$ , and  $\text{CaSO}_4$ . The buildup in Plant B consisted primarily of CaO,  $\text{CaCO}_3$ , and spurrite plus smaller quantities of  $\text{SiO}_2$ ,  $\text{C}_{12}\text{A}_7$ , KCl,  $\text{C}_2\text{S}$ ,  $\text{CaSO}_4$ , and calcium langbeinite. The temperature of the gas leaving a fourth stage is usually about 1075 K, and the gas temperature entering the cyclone is typically above 1275 K. These temperatures span the range over which alkali chloride vapors condense to the liquid state. Therefore, under these conditions it is reasonable to expect chloride condensation in the fourth stage of the preheater. Laboratory experiments showed that the alkali chlorides, KCl and NaCl, are very effective catalysts in the formation of spurrite. Tests on the Plant A buildup suggested that it contained more spurrite than Plant B buildup because it was much richer in alkali chlorides. Subsequent tests with the kiln dusts given in Table 3-6 confirmed that spurrite formed only from Dust L which contained 6.24 percent chloride, compared to all the other dusts which contained less than one percent Cl. Laboratory tests also showed that a temperature of about 1075 K, which is the temperature in the fourth stage of the preheater, is required for this reaction to take place. It is believed that the  $\text{CaCO}_3$  (calcite) buildup in Plant A was due to the recarbonation of CaO in situ. The anhydrite,  $\text{CaSO}_4$ , was probably formed as a result of a reaction between CaO or  $\text{CaCO}_3$  from the raw feed and  $\text{SO}_2$  from the kiln gases.

Buildups in the kiln formed at the feed end of the kiln are very similar to those formed in the fourth stage of the preheater. On the other hand, buildups near the kiln exit have a composition very similar to that of the clinker. Bhatti (Reference 3-8) has reported the analysis of one kiln buildup near the feed end of the kiln. This particular buildup contained primarily spurrite (more than 55 percent by weight) and also a large amount of sulfate spurrite (calcium silicosulfate). It contained only a small amount of  $\text{CaCO}_3$ , indicating that most of the CaO had combined with  $\text{SiO}_2$  and sulfur to produce the large quantities of the two types of spurrite. The deposit also contained small amounts of  $\text{CaSO}_4$ , calcium langbeinite,  $\text{K}_2\text{SO}_4$ , and KCl. Buildups formed

at the exit of the kiln are not of particular interest here because, strictly speaking, the processes taking place within the kiln do not fall under the domain of heat recovery. However, Bhatti has presented some important results on the buildup formed on dolomite brick in the burning zone of a kiln. Of particular interest here is the buildup which occurred nearest the refractory lining. This inner layer contained about 20 percent alkali sulfate, primarily  $K_2SO_4$ . It was speculated that the deposition of the alkali sulfate in the pores of the dolomite brick could have initiated formation of the deposit. Initially the vapor could have penetrated the cores of the brick, condensing to a liquid or a solid on the outer surfaces near the kiln shell.

Bhatti summarized his findings by suggesting several steps which could be taken to eliminate or reduce the buildup problems which were observed. First, the use of materials in the raw feed which contain excessive quantities of chloride or sulfur compounds should be reduced or eliminated. Second, if possible, the use of high sulfur coal should be avoided. Third, calcium chloride,  $CaCl_2$ , should not be used to prevent the freezing of coal in the winter in cold climates. Fourth, in preheater systems a kiln bypass system should be used to limit the levels of chlorides, alkalies, and sulfur in the kiln. Fifth, the use of coals with high ash content and low ash fusion temperatures should be avoided. Sixth, the kiln and preheater conditions -- such as temperature, pressure, feed rate, etc. -- should be monitored in order to detect the formation of buildups during their early stages. Finally, excessive cooling of the kiln shell should be avoided; in fact, in some cases buildups can be dislodged by insulating the kiln shell where the buildup has formed.

Strict control of the constituents in the raw feed and the coal, including the ash, is somewhat difficult because of the variation in both of these quantities. The kiln bypass in the preheater systems has proved to be a very effective way to eliminate chlorides, sulfates, and alkalies as was discussed earlier. The possible monitoring of the kiln and preheater surface temperatures deserves some further consideration. In fact, Coplay Cement of Nazareth, Pennsylvania, has installed an infrared scanning system to continuously monitor the shell temperature of rotary kilns. An AGA Cemscanner continuously monitors the kiln shell, which is 85.3 m long and 5.49 m wide, on

a 24 hr, seven days a week basis. When the detector registers a sharp increase in temperature, indicating that a coating has dropped off the kiln wall, high-powered fans are used to cool the shell in order to promote the building of a new coating to prevent possible further brick damage. A similar procedure could be used to detect buildups, by noting a drop in surface temperature, in the kiln and also in the preheater. Thus, costly unscheduled shutdowns, along with the loss of production, could be avoided or at least minimized. (Reference 6-1).

Chistyakova and Milhaylov (Reference 6-2) have reported chemical analyses of several deposit samples taken from a preheater system. The kilns were fired with a mixture of coal and gas shale and the raw material included fine coke, a waste product from the gas-shale industry. The region of maximum fouling occurred in the zone between the upper end of the kiln and the first-stage cyclone. In general, the analyses showed -- in comparison to the raw feed -- that the deposits were rich in alkalies, sulfates, and chlorides. Although the discussions in Reference 6-2 are quite brief, and somewhat sketchy in places, some general results were obtained which are of interest here. In the sample analyses which were carried out, it was found that in general the deposits were basically of multicomponent character and that they contained primarily the following constituents:  $K_2SO_4$ ,  $KCl$ ,  $K_2Ca_2(SO_4)_3$ ,  $CaSO_4$ ,  $C_2S$ ,  $CaO$ ,  $CaCO_3$ , and  $C_3A$ . Smaller quantities of sodium sulfates and chlorides were also present, along with an iron-containing phase. Specifically, one deposit contained more than 40 percent  $K_2Ca_2(SO_4)_3$ , and a second deposit consisted of up to 50 percent  $K_2SO_4$ . Chistyakova and Milhaylov concluded as a result of their findings, that a reduction in the amounts of alkali chlorides and sulfates in the feed and in the fuel could overcome this problem of fouling. They also suggested a modification in the design of the heat exchangers in order to reduce the process of coating formations, but did not give any specific details.

Apparently, based on operations in Europe, the counterflow preheater described in Section 4-1 has experienced no downtime as a result of buildup problems. (References 6-3 and 6-4). The manufacturers claim that this type of preheater is not subject to fouling deposits because of the large cross-sectional areas of the tube in which any incipient buildups fall off as a

result of their own weight before the deposit has a chance to age and become tenacious. They also claim that because of the specific design of the preheater, the sticky particles become entrained by the kiln gases and hence do not deposit on the walls of the preheater. However, in spite of the successful operating experience of the counterflow preheater in European applications, a critical evaluation of the performance of this type of preheater in high alkali feeds, such as found in certain parts of the U.S., is not available.

## 6.2 GAS-TO-AIR HEAT EXCHANGERS

Smith Engineering Company has built 32 gas-to-air units which are presently in operation in clinker cooler vent line exhausts throughout the United States. The volumetric flowrates for these units range from a low of  $5.66 \text{ m}^3/\text{s}$  to a maximum of  $59.5 \text{ m}^3/\text{s}$ . Except for some erosion and flow maldistribution problems, caused by poor header design in one case and flow at an angle to the tubes in another case, these units have operated very successfully. There is no evidence of any fouling problems in these units, probably because the clinker dust is very abrasive and tends to clean the inside of the tubes as the exhaust gases flow through the tubes. The replaceable sleeves described in Section 4 adequately handle erosion problems near the inlet of the tubes.

Smith Engineering has one gas-to-air unit installed in the bypass loop of a suspension preheater system. This exchanger is located at the Cementos Mexicanos plant near Mexico City, Mexico. The gases leave the preheater at a temperature of about 1255 K and are quenched with cool air to a temperature of 755 K. Thus, the inlet gases to the heat exchanger have a temperature of about 755 K and are cooled in the exchanger to about 535 K before entering a baghouse. Even though the gases are heavily laden with alkalis, there has been no evidence of any fouling inside the tubes. Probably the reason no difficulties have been encountered is because the maximum gas temperature of 755 K is below the temperature range of 865-920 K at which the alkalis become sticky. This unit has apparently not been operated in the 865-920 K temperature range, either accidentally or intentionally.

A very interesting problem has been encountered in a heat exchanger operating at the Monarch Cement Company, Humboldt, Kansas. The gas-to-air unit, manufactured by Smith Engineering Company, was installed in the downcomer between the suspension preheater exit and the induced draft vent fan. The purpose of this exchanger is to cool the preheater exhaust gases, thus reducing the amount of bleed air required. This exchanger has 0.0762 m diameter tubes, 6.71 m tubelength, and 616 tubes arranged on an inline layout. The unit is rated at about 5280 kW with a volumetric flowrate of 19.6 m<sup>3</sup>/s. The exhaust gases enter the top of the exchanger and flow vertically downward inside the tubes. Operation of the exchanger resulted in the buildup of a 3.18 mm-thick deposit in a very short period of time. However, after reaching this thickness, the deposit essentially remained at this thickness, i.e., a condition of asymptotic fouling was reached. This insulating layer reduced the heat transfer by a factor of about two, and increased the pressure drop by a factor of about three. Four vibrators (ESP rappers) and a sonic horn were installed in an attempt to remove the deposit without success. At one point it was thought that the formation of sticky CaSO<sub>4</sub> salts was a contributing factor. However, very detailed chemical analyses led to the conclusion that there was no evidence of any chemical reaction or that the physical or chemical characteristics of the dust were responsible for the buildup. Measurements indicated that the dust was very fine with over 25 percent of the dust particles less than 2.1 μm in diameter and over 50 percent of the dust less than 4.2 μm in diameter. Owing to the 3.18 mm-thick buildup, and the associated operating problems, the heat exchanger was taken offstream and was allowed to sit idle for about 9 months. Sometime during this nine-month period, it was later discovered that the deposit dropped off the tubes and fell to the bottom of the exchanger. When the exchanger was put back in service it fouled just as before in a matter of a few hours. Thus, based on the chemical and physical analyses which were carried out, it is believed that static electricity is the basic deposition mechanism in this particular problem (Reference 6-5). However, since over 50 percent of the deposited particles were less than 5 μm in diameter, it is also possible that thermophoresis could have been a contributing transport mechanism in this case. However, a more detailed study of this phenomenon would be required to determine with greater certainty whether the deposition mechanism was indeed one of combined electrophoresis and thermophoresis.

Another Smith Engineering gas-to-air heat exchanger was installed at the Kaiser Cement and Gypsum Corporation plant in Permanente, California. It was installed such that the preheater exhaust gases could be: (1) routed directly to the heat exchanger for cooling prior to entering a dust collector, or (2) used to preheat the material in the grinding mill when the raw mill was operating. In the latter mode, the exhaust gases passed successively through the raw mill, a cyclone separator to remove particulates, an induced draft fan, and then to the heat exchanger, after which the gases went to the dust collector. In this loop the exhaust gases normally entered the heat exchanger at a temperature of about 395 K and left at about 320 K. However, since the gases had a considerable amount of moisture in them, water condensed onto the cool tube surfaces which attracted kiln dust, and the tubes became plugged very quickly. Unfortunately, this particular system did not include a bypass loop around the heat exchanger which could have been utilized at appropriate times to alleviate this problem.

At the Martin Marietta Cement plant in Davenport, Iowa -- which went onstream in December 1981 -- a gas-to-air heat exchanger is operating in the preheater exhaust stream. This particular unit has 0.102 m diameter tubes and was manufactured by American Air Filter Company, Inc., Louisville, Kentucky. There has been some plugging of the tubes in this exchanger which is known to be operating in a situation with high levels of both  $\text{SO}_2$ , resulting from the sulfur in the coal, and moisture so it is likely that  $\text{CaSO}_4$  is being formed in the exhaust gas stream. Also, there has been some evidence of mild corrosion of the tubes, but no pitting has been observed. Presently, the gas-side fouling problem is being handled by the use of sonic soot blowers, activated about every 15 minutes on a continual basis (Reference 6-6).

A gas-to-air heat exchanger in a preheater exhaust application has recently been installed at the California Portland Cement plant in Mojave, California. This exchanger, which has 0.0762 m diameter plain tubes 9.14 m long, was manufactured by Tera Engineering Company, Santa Fe Springs, California. It is known that the exhaust gases in this installation contain  $\text{SO}_2$  and large amounts of water vapor. Although random plugging of a few tubes has occurred to date, the problem is not serious and the heat exchanger is operating successfully (Reference 6-7). This particular exchanger has the

unique feature that a portion of the hot exhaust air is recycled and mixed with ambient air so that the air temperature entering the unit is about 340 K, rather than at ambient conditions. A very large surface area of 4460 m<sup>2</sup> has been incorporated into the exchanger to ensure that the desired outlet gas temperature is achieved. The elevated-inlet-air-temperature design ensures a sufficiently high inside tubewall temperature throughout the heat exchanger so that the acid and water dewpoint problem is avoided (Reference 6-8).

### 6.3 WASTE HEAT BOILERS

The Riverside Cement Company, recently purchased by the Gifford-Hill Company, has been generating electrical power for over 25 years using waste heat boilers (References 6-9 and 6-10). Based on this successful operating history, the decision was made to convert two, two-stage preheater kilns to waste heat boiler systems to generate electricity. The boilers are rated at 955 K and 4.83 MPa and were supplied by the Deltak Corporation, Minneapolis, Minnesota. Each boiler was also equipped with an economizer and a superheater. In the superheater section, which is of principal interest here, the tubes are 0.0508 m diameter, the transverse pitch is 0.127 m, and the longitudinal pitch is 0.152 m with an inline layout. On initial operation of the system, the gas passages in the superheater section of the boiler became plugged with a hard, glass-like deposit in a matter of just a few days. The heaviest deposit was in the first three rows and resembled that shown in Figure 5-2. In order to clean the heat exchanger surfaces, the material was chiseled out manually. At the same time, the gas temperature entering the superheater was about 1060 K. Experience with the existing waste heat boilers had demonstrated that a gas temperature much above 980 K would cause plugging of the boilers. It is believed that the mechanism causing this particular type of fouling is condensation or de-sublimation of potassium sulfate and sodium sulfate, processes which occur about  $1045 \pm 6$  K (Reference 6-11). Although both systems were initially equipped with rotary sort blowers, they were removed after one of them turned out to be defective. An attempt was then made to install additional chains in the kilns to bring the gas temperature down to the 950 K design value. However, this approach was apparently not entirely successful; therefore, at the present time an evaporative gas cooling system manufactured by Sonic Development Corporation, Mahwah, New Jersey, is being installed just

upstream of the superheater section. This system will maintain the gas temperature at a level below the sulfate de-sublimation temperature by modulating the degree of superheat in the economizers (Reference 6-11).

The gas-side fouling mechanism in this particular case appears to be very similar to the sodium sulfate deposition mechanism reported in Reference 5-29 and described in Section 5.3. It will be recalled in that study that at 1045 K (772 C), the  $\text{Na}_2\text{SO}_4$  deposition rate was close to a maximum value. Thus, it would be expected that a drop in the gas temperature would reduce the wall temperature and hence the deposition of the alkali sulfates as shown in Figure 5-3. Thus, the proposed evaporative gas cooling system should eliminate or at least reduce the gas-side fouling problems which have been experienced at the Riverside Cement Company.

The St. Lawrence Cement Company, with support from the Canada Energy, Mines and Resources, has recently undertaken a project to achieve major energy savings in their cement plant at Mississauga, Ontario, Canada (Reference 2-3). One phase of this project involves waste heat utilization to generate electricity. The waste gas stream utilized was the preheater exhaust which was laden with dust to the extent of  $20\text{--}30 \text{ gNm}^{-3}$ . It was anticipated that these gases could cause erosion and/or fouling of heat exchanger surfaces; therefore, a preliminary study was carried out to investigate the potential problems. A small-scale heat exchanger was constructed with six carbon steel tubes: two plain tubes, two externally finned tubes with 78.7 fins/m and two externally finned tubes with 157 fins/m. The dimensions of the tubes were not given in the report. The tubes were mounted in a crossflow arrangement with the dirty gas flowing on the outside of the tubes and cool air on the inside of the tubes. The tubes were individually instrumented to measure the inlet and outlet air temperatures, inside wall temperature, and exhaust gas temperature. Thus, the temperature measurements were used to monitor the effects of gas-side fouling. The kiln was in continuous operation for a month, and during this time temperature measurements were taken at regular intervals. Gas temperatures ranged from about 570 to 630 K, with corresponding average wall temperatures of about 355 to 520 K. Based on these measurements, it was determined that the effect of fouling was negligible on all the tubes during the entire course of the study. Interestingly, the tubes were covered with a



fairly thick layer of dust upon completion of the tests. However, it was discovered that this dust was very loosely deposited and could easily be removed by either blowing air over the tubes or by vibrating them slightly. Thus, it was concluded that this material could not have been on the tubes during the tests and undoubtedly was deposited as the tubes were cooled during the shutdown operations. A visual inspection of the tubes indicated that no significant corrosion or erosion problems had occurred during the month-long study.

The National Gypsum Company plant in Alpena, Michigan, generates electricity using plain-tube waste heat boilers. Nine long-dry process kilns, fired using coal as the fuel, are currently in operation at this site. The use of waste heat boilers at this plant is due in part to the kerogen content of the local shale which is used as one of the raw materials. National Gypsum has a cogeneration agreement with the local electric utility which allows them to sell electricity which is produced in excess of the requirements in the cement plant. Although some gas-side fouling problems have been experienced in the past at this plant, steam soot blowers are presently being used on a regular basis with no gas-side fouling problems.



## SECTION 7

### DELETERIOUS EFFECTS OF GAS-SIDE FOULING IN CEMENT PLANTS

There have been very few attempts to quantify the deleterious effects of any type of fouling. The major problem is the number of uncertainties involved in such an analysis. As Thackery (Reference 7-1) has pointed out, such efforts basically become a series of "considered guesses" because of the many unknowns. However, Reference 7-1 is undoubtedly the best and most comprehensive contribution in this area. Thackery's analysis includes the cost of all types of fouling in the United Kingdom and attaches an estimated cost in British pounds to each of the associated costs. The purpose of this section is to consider the deleterious effects of gas-side fouling in U.S. cement plants, including corrosion and erosion, and to estimate the related costs in present U.S. dollars.

The deleterious effects of fouling in cement plants may be broken down into the following categories:

- (1) Increased capital costs.
- (2) Increased maintenance costs.
- (3) Loss of production.
- (4) Energy losses.

Each of these items will be considered in more detail.

Increased capital costs result in part from oversizing equipment to account for the anticipated fouling. First, the fouling layer produces a thermal resistance because of its relatively low thermal conductivity. This resistance, in turn, requires a larger surface area for a given heat transfer requirement. Gas-side fouling factors are not well known at the present time, so excessively large safety factors can result in very conservative designs. Second, because of reduced flow passages due to the fouling layer, an increased pressure drop is produced. Therefore, capital expenditures are required for larger fans because of the larger power requirements. In some cases, capital

cost increases because of increased pressure drop can be as large or larger than those due to oversurfacing because of reduced heat transfer. Third, in those situations where on-stream cleaning of the heat transfer surfaces is required, there are capital costs associated with the provision for cleaning equipment.

The next item to be considered is that of increased maintenance costs. The major factor here is the cost of cleaning. In waste heat boilers sootblowers are generally used for cleaning purposes using either steam or air. Sonic devices show some promise for the future, especially for light, fluffy deposits. In a somewhat unique application, Riverside Cement Company is using a continuous water spray system to reduce the exhaust gas temperature and thus prevent the condensation of sulfate-type deposits on the boiler tubes. If at all possible, cleaning is done onstream. However, in the event the system must be shut down because of gas-side fouling problems, there will be maintenance costs associated with the manual cleaning of the heat transfer surfaces. For example, such maintenance procedures are used routinely in the maintenance of suspension preheaters. Additional maintenance costs will also be incurred when trouble shooting gas-side fouling problems and in carrying out the associated chemical and related analyses.

The loss of production can be a very significant factor depending on the nature of the specific problem. Downtime or operation at reduced capacity due to gas-side fouling can result from buildups in suspension preheaters, in the kiln, or in the various heat exchangers described in Section 4. In addition to the loss of finished product during the actual downtime, several days will usually be required for transient cooling on shutdown and heating on startup. The trend toward centralized computer control systems in the cement industry is helping to reduce loss of production by sensing potential buildup problems. In some cases the difficulties can be overcome while the system is still onstream. One very serious problem in the cement industry which can cause costly downtimes, as well as extensive damage to plant equipment, is coal dust explosions. A panel discussion on this subject was held at the 1981 International Cement Seminar. Typically, this problem can occur when returning onstream after an upset produced by a power outage. The problem can also occur if pulverized coal is added in the absence of feed. Buildup of coal dust can

take place in flash calciners and several fires have also occurred in baghouses. Important parameters include coal moisture, volatility, and particle size. Although loss of production in general is a very difficult item to quantify, it is clearly a very important factor.

The final item to be considered here is energy losses due to gas-side fouling. The obvious items are energy losses due to reduced heat transfer and increased power requirements because of larger pressure drops. However, in addition to these factors, a more serious consideration is that of dumping dirty gas streams because of the potential for gas-side fouling in heat-recovery systems, along with the associated problems of maintenance and loss of production. An important related factor is the need, or lack of need, for the recovered energy. In other words, given that a hot exhaust stream is available, if there is no pressing need for the recuperated energy it will not be utilized, irrespective of potential gas-side fouling problems. However it is clear, as was seen in Table 3-5, that there is a considerable amount of energy which is being exhausted from U.S. cement plants. In the following analysis, this energy will be quantified, and an estimate will be made as to the fraction which is not being utilized because of potential gas-side fouling problems.

Consider Table 7-1 where the information from Table 3-1 has been recast in the form shown. In order to estimate the value of the energy in the various exhaust streams which are not being utilized in cement plants, the following approach was taken. For each stream the temperature level and total energy content on an annual basis were established from Table 3-1. It was then assumed that for each of these streams a Rankine bottoming cycle, utilizing either a steam or an organic fluid boiler, could drive a turbine to produce electrical power which can easily be quantified by assuming a conversion efficiency. For computational purposes, it was assumed that the conversion efficiency varied linearly from a value of zero at 310 K to 35 percent at 810 K with a maximum efficiency of 40 percent. Using the current industrial cost of electrical energy in the U.S. at \$0.045 per kW-hr (Reference 7-2), it is thus possible to place a dollar value on each of the four streams in Table 3-1. The results of this analysis are summarized in Table 7-1. Only those streams with temperatures of at least 535 K were

Table 7-1. Estimated Value of Energy in U.S. Cement Plant Exhaust Gas Streams

Process	Exhaust Gas Source	Approximate Temperature K	Total Annual Clinker Capacity Short Tons	Total Energy Content kW-hr	Rankine Cycle Efficiency	Value in Current U.S. Dollars**
Wet	Kiln Exit	535	42.6 x 10 <sup>6</sup>	1.62 x 10 <sup>10</sup>	0.156	\$114 million
Long-Dry	Kiln Exit	865	23.6 x 10 <sup>6</sup>	1.04 x 10 <sup>10</sup>	0.389	182 million
Preheater	Preheater Exit	645	20.2 x 10 <sup>6</sup>	0.36 x 10 <sup>10</sup>	0.233	38 million
	Bypass*	1285	20.2 x 10 <sup>6</sup>	0.11 x 10 <sup>10</sup>	0.400	20 million

\*Bypass calculated assuming a 10 percent bypass

\*\*Computed at the rate of \$0.045 per kW-hr

included in the analysis; thus, the clinker cooler, finish mill, and separator exhausts have been neglected here.

An attempt will now be made to estimate the percentage of each item listed in Table 7-1 which may be attributed to the potential of gas-side fouling. First, the bypass gases are heavily laden with alkalies, chlorides, and sulfur; therefore, very little effort has been made to recover this energy because of the gas-side fouling and corrosion potential. Thus, the entire total of \$20 million may be attributed to potential gas-side fouling problems. Second, the kiln exhausts from long-dry process kilns have a high moisture content and are generally not used to dry raw materials. In fact, auxiliary fuel heating, primarily from natural gas and fuel oil, is sometimes used to dry the raw materials in these kilns. As was discussed in Sections 4 and 6, there are presently four cement plants in the U.S. which utilize long-dry kiln exhausts to produce electrical power using waste heat boilers. However, these plants use only about 10 to 15 percent of the available energy in such plants. The lack of utilization of the energy from this stream is

due to economics and other considerations as well as the potential of gas-side fouling. Thus, it will be assumed that only 20 percent, or a total \$36 million, of the total of \$182 million may be attributed to the potential of gas-side fouling. Third, exhausts from wet process kilns are available at about 535 K. Due to the high moisture content of the gases (ranging from about 30 to 40 percent) plus the presence of sulfur compounds, both water and acid dewpoints are potential problems, especially at lower temperatures. Apparently very little, if any, use is presently made of these streams. Thus, it is assumed that 50 percent, or \$57 million, of this stream is lost because of fouling and corrosion potential. Fourth, the preheater exhaust gases are available at 645 K. These gases are often used for drying materials during the milling operation, but only after gas-to-air heat exchangers or evaporative spray coolers are used to reduce the temperature. However, the kiln exhaust gases mix/react well with the limestone in the raw materials during the preheating process so that the concentration of sulfur compounds is lower than in either the wet or long-dry process. However, as was discussed in Section 6, there have been gas-side fouling problems in several gas-to-air heat exchangers utilizing preheater exhausts. Therefore, for this stream 20 percent or a total of \$8 million is estimated to be due to gas-side fouling potential. Thus, the sum of these four streams which is not being utilized because of gas-side fouling and corrosion potential is estimated to be \$121 million, or approximately one-third of the total rejected energy in the exhaust gas streams.

Estimates will now be made as to the annual loss of production costs, increased maintenance costs, and capital costs because of gas-side fouling. The current retail price of cement in the greater Los Angeles area is \$5.90 per 94 lb bag (Reference 7-3). The current production of portland cement clinker in the U.S. according to Table 2-3 is 86 million tons. Adding an additional five percent for the constituents mixed to the clinker (primarily gypsum) to make cement gives a total of 90.3 million tons of portland cement produced in the U.S. per year. If a very conservative estimate of one percent loss in production due to downtime resulting from gas-side fouling is made, these costs total \$108 million. The cement industry is increasing its capacity by 3 to 4 percent per year over the next several years (Reference 2-4). Although most of the new kilns are of the preheater type, at least one company -- the California

Portland Cement Company -- is planning for waste heat boiler systems on two kilns. Taking into consideration oversized equipment for new plants, provision for onstream cleaning, sensors and controls, and modification of existing equipment, it seems reasonable to assume that \$5 million in capital costs will be expended each year because of the potential of corrosion, erosion, and gas-side fouling problems. Finally, increased maintenance costs due to gas-side fouling are difficult to estimate. However, using Thackery's estimate that fouling maintenance costs are about 80 percent those of increased capital costs gives a total of \$4 million annually. This amount seems to be a reasonable estimate for onstream cleaning, offstream cleaning and repairs, trouble shooting, and related analyses. Thus, the total estimated annual costs for gas-side fouling in cement plants in the U.S. are given in Table 7-2. It should be emphasized that the total estimated costs have a great deal of uncertainty associated with them. However, in most cases the estimates have been conservative so that if these figures are in error, they are probably on the low side. In any event, the total estimated costs represent an annual cost of about \$0.24 billion. It should also be pointed out that in the energy loss total, most of the exhaust gases are not presently being used because there is no pressing need in the cement plants for the energy which would be recovered.

Table 7-2. Summary of Estimated Annual Costs in U.S. Cement Plants Due to Gas-Side Fouling, Corrosion, and Erosion

Type of Cost	Estimated Cost
Capital Costs	\$ 5 million
Maintenance Costs	4 million
Loss of Production	108 million
Energy Losses	<u>121 million</u>
Total	\$238 million



However, as time goes on and energy costs continue to rise, there will be continuing interest and economic pressures to recover as much of this energy as possible. Since this energy will not be needed in the cement plants per se, and since the temperature levels of the streams are appropriate for either steam or organic Rankine cycles to produce electricity, it appears that waste heat boilers will become popular in the cement industry once again. As this trend takes place in the cement industry in the years ahead, it will become apparent at that time with much greater certainty as to the associated problems and costs of gas-side fouling. Clearly, any major technological developments in mitigating the effects of gas-side fouling at the present time will help to speed heat-recovery efforts in the cement industry in the future.



## SECTION 8

### CONCLUSIONS AND RECOMMENDATIONS

The purpose of this section is to summarize the major findings in this study, present both short-term and long-term recommendations for further study, and make some concluding remarks.

#### 8.1 SUMMARY OF MAJOR FINDINGS

The cement industry is the most energy-intensive industry in the U.S. in terms of energy cost as a percentage of the total product cost. There is considerable potential for heat recovery in the cement industry, but this potential is far from being achieved, in part because of gas-side fouling problems. This study has concentrated on the characterization of exhaust streams, heat-transfer equipment, gas-side fouling mechanisms, and gas-side fouling experience in the cement industry. Some attention has also been devoted to the deleterious effects of gas-side fouling in U.S. cement plants. The major conclusions reached in this study are summarized in this section.

##### Characterization of Waste Heat Exhaust Streams

At the present time 87 percent of the cement plants in this country are using coal as the primary fuel. With the cost of oil and gas expected to increase more rapidly than coal, it is expected that this trend toward coal will continue. The principal raw materials used in making cement typically include  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ , and  $\text{Na}_2\text{O}$ . In addition to carbon, oxygen, hydrogen, nitrogen, and sulfur, the coal usually contains about 8 to 10 percent ash, which includes primarily the constituents  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  with smaller quantities of  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{SO}_3$ . The exhaust streams in cement plants which have the greatest potential for heat recovery include the kiln exit gases, the clinker cooler vent gases, and in the case of the preheater process, the preheater exit and the bypass exhaust gases. These exhaust streams range in temperature from 410 to 1285 K, are generally dusty, and in the case of clinker cooler exhaust highly abrasive. In preheater

systems the kiln bypass gases are highly contaminated with alkalies, sulfates, and chlorides. Since the content of both the coal and the raw materials can vary significantly, depending on the physical location, the actual content of the exhaust gases also varies somewhat. However, in general, kiln dusts typically consist of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{SO}_3$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{TiO}_2$ , F, and Cl. Particle size distributions range from molecular size to about 75  $\mu\text{m}$ . The density of particulates, which is important in deposition by particle impaction, can be very large and ranges up to 15000 times that of the gases which are carrying the particulates. Although the specific constituents of the gases are known reasonably well, very little characterization of the exhaust gases has been done at the actual operating temperatures. A knowledge of the actual state of the various particulates at elevated temperatures would be useful in trying to get a better understanding of the various particulate fouling transport, attachment, and removal mechanisms. Also, such information would be valuable in trying to understand the various chemical reactions and the rates at which they take place.

#### Heat-Transfer Equipment

The major types of heat-transfer equipment used in the cement industry include: preheaters, gas-to-air heat exchangers, waste heat boilers, and clinker coolers. The trend in this country is toward the use of suspension preheaters in which the raw feed in finely ground form is preheated in a series of cyclones by the hot kiln exhaust gases. Gas-to-air heat exchangers are used primarily to control the air temperature of the clinker cooler vent exhaust gases and to a lesser extent the preheater exhaust gases before these gases are cleaned and discharged to the atmosphere. Four plants in the U.S. presently generate electricity from kiln exhausts using steam waste heat boilers.

Finally, clinker coolers are used to cool the clinker quickly in order to obtain a superior cement upon grinding of the clinker. A portion of the high-temperature air from the clinker coolers is recuperated and used as secondary combustion air in the kiln. In some cases part of the air heated by the clinker cooler is also used in the precalciner of Secondary Furnace type preheater systems.

The present state-of-the-art is such that only plain tubes are being used in tubular heat exchangers. Thus, even though both the gas-side and air-side heat transfer coefficients are quite low, neither fins nor any other type of enhancement is presently being used in heat-transfer equipment in the cement industry. It appears that the potential for fouling on the gas-side is the single most important factor in this situation. In general, gas-side fouling factors are not known with any degree of certainty at the present time. Thus, the tendency is to use large fouling factors for design purposes which results in conservative and hence oversurfaced heat exchangers.

### Gas-Side Fouling Mechanisms and Experience

A review of the basic fouling mechanisms indicates that particulate fouling, chemical reaction fouling, and corrosion fouling can all be important to some extent in the heat-transfer equipment used in cement plants. In the case of particulate fouling, the mechanisms by which the particles are transported to the surface are very important. For very small particles laminar or Brownian diffusion, thermophoresis, and electrophoresis are most important transport mechanisms, while for the larger particles turbulent mass transfer and inertial impaction become very important. For example, it appears that electrostatic forces are very important when preheater exhaust gases pass through a heat exchanger. However, in general, the importance of these various transport mechanisms as a function of parameters such as gas velocity, gas temperature, surface temperature, and surface material is not well known. Also, the relative importance of each phenomenon under conditions when combined transport mechanisms can occur is understood to an even lesser extent. Several deposition models have been proposed in the literature to predict transport to the wall, but it still is not very well understood why some particles stick to the surface and others do not. Much less is known about basic removal mechanisms since removal has been studied even less than deposition. Clearly, there is a need for a fundamental study in the area of particulate fouling including a consideration of transport, attachment, and removal mechanisms. The ultimate objective of this study is to formulate a general model which can accurately predict these mechanisms over a broad range of parameters.

Certain constituents from both the feed and the ash in the coal tend to be troublesome from the standpoint of chemical reaction gas-side fouling.

These constituents include the alkalies, sulfates, and chlorides. The mechanism of deposition of  $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  can be a problem in the temperature range of about 675 to 1075 K and can cause severe fouling in certain situations. The presence of iron oxide is necessary for the catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  which in turn combines with  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$  to form an alkali sulfate. Although some work has been done in this area, there needs to be a better understanding of this mechanism, especially as a function of the concentration of both the alkalies, the concentration of other constituents, and the parameters of velocity, temperature, and surface material. Another deposit which can be serious, especially in preheaters, is that of spurrite,  $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$ . The formation of this compound is catalyzed by the presence of  $\text{KCl}$  and  $\text{NaCl}$ . In some cases  $\text{CaO}$  can recarbonate in situ which gives the deposit hardness and strength. Other troublesome deposits which occur under moderate to high temperature conditions are  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CaO}$ ,  $\text{CaCO}_3$ , and  $\text{CaSO}_4$ . In some cases these deposits are formed with a liquid surface which tends to attract particulates from the gas stream.

If the gas stream contains large quantities of water vapor, as is frequently the case, the  $\text{SO}_3$  can combine with water to form  $\text{H}_2\text{SO}_4$ . If the surface temperature drops below about 450 K, there is the danger that the sulfuric acid, water, and other condensables will deposit onto the heat transfer surfaces. In addition to causing a potential corrosion problem in such cases, the wet surface can also attract particulates which can plug a heat exchanger rapidly under certain conditions.

However, it is known that the alkaline earths can mitigate the effects of gas-side fouling deposits to some extent. In particular, kiln gases typically contain small percentages of  $\text{MgO}$  and larger quantities of  $\text{CaO}$  which is, after all, the primary constituent in the cement. In fact,  $\text{MgO}$  additives have been used for some time to mitigate the effects of gas-side fouling in coal-fired furnaces and boilers. The inhibiting effect is achieved as a result of  $\text{CaO}$  or  $\text{MgO}$  combining with  $\text{SO}_3$  to form either calcium or magnesium sulfate. These sulfates can in turn react with the alkali sulfate to form an alkali (or magnesium) trisulfate complex. Experience has shown that sufficient lime to control sulfur oxides produce a softer, more friable deposit which is relatively easy to control with soot blowers. Interestingly, corrosion does

not appear to be a serious problem in the heat exchangers used in cement plants. A lack of this problem may be due to the presence of MgO and CaO but additional analyses are required to confirm this hypothesis. Although there has been some progress in obtaining a better understanding of the important chemical reaction fouling mechanisms in cement plants, additional work is required to quantify these phenomena as a function of the important parameters including chemical composition of the gas, gas temperature, surface temperature, and gas velocity. Deposit analysis would be expected to provide a considerable amount of information in such a study. Techniques which would capitalize on the beneficial effects of MgO and CaO would be especially desirable. Also, some consideration must be given to particulate fouling and chemical reaction fouling under conditions when they occur simultaneously.

In spite of the fact that exhausts in cement plants, especially from the clinker cooler, contain large quantities of particulates, it appears that erosion does not cause too much difficulty. In particular, the problem of erosion near the inlet of circular tubes is being handled through the use of a removeable sleeve which is five diameters long. After the exhaust gases enter the tube, erosion does not appear to be a major problem. This is perhaps not too surprising since previous studies have shown that for ductile materials such as steel the critical impingement angle is about  $30^\circ$ . Since the velocity vector inside the tube is essentially parallel to the tube axis, the impingement angle is close to zero and hence very little erosion results. Near the tube inlet where the impingement angle can be near  $30^\circ$ , the sleeve insert sustains the brunt of the erosion.

The standard procedure for cleaning boiler surfaces is by means of steam soot blowers, and this technique is being used in waste heat boilers in cement plants. Recently there has been considerable interest in the use of sonic horns to remove gas-side fouling deposits from various heat exchanger surfaces, but the effectiveness of these devices has not been established and is not well understood. Other cleaning techniques, such as vibrators, are also available and should be explored further. A study should be undertaken to investigate the effectiveness of various cleaning devices with the objective of matching a particular type of cleaning device with a particular type of fouling deposit.

In recent years there has been a trend toward computerized control in the cement industry. By monitoring critical parameters such as gas temperature, upsets and other potential problems can be detected early enough to avoid shutdowns or at least minimize production interruptions. One problem of major concern is that related to the accumulation of pulverized coal and hence the potential for explosions and fires. Another area of considerable potential which has been exploited very little is the use of infrared thermography to detect buildups in preheaters and kilns. In many cases, if buildups are detected early enough, potential problems can be minimized or perhaps avoided altogether.

### Deleterious Effects of Gas-Side Fouling

The deleterious effects of gas-side fouling in cement plants are due to: (1) increased capital costs, (2) increased maintenance costs, (3) loss of production, and (4) energy losses, with the major losses attributed to Items 3 and 4. A good portion of the energy losses are due to the potential of gas-side fouling, i.e., because of the possibility of fouling, no attempt is made to recover the energy in the hot exhaust gases because of the anticipated fouling problems. An additional factor is that because most of the electrical energy required is now satisfied with the purchase of electricity, there would be basically very little need for this energy in the plant, even if it were recuperated. For the same reason, plus the potential dewpoint problem, very little effort has been made to recover energy from exhaust gas streams with a temperature of less than about 535 K. Although difficult to quantify, the loss of production as a consequence of gas-side fouling can be a very significant factor. An order of magnitude analysis, which admittedly is on the conservative side, shows that the annual estimated cost of gas-side fouling in U.S. cement plants is on the order of \$0.24 billion.

## 8.2 RECOMMENDATIONS FOR FURTHER WORK

Based on the findings of this study, as summarized briefly in the preceding section, it is apparent that additional work must be undertaken if the various gas-side fouling mechanisms in cement plants are to be understood and brought under satisfactory control. Several projects are proposed as



listed below, broken into two categories: (1) short-term projects which would be expected to be resolved in about three years, and (2) long-term projects which would probably take from 3 to 10 years to overcome. The projects are essentially self-explanatory, when taken in the context of the discussion presented in Section 8.1, and are listed in order of priority. Although some of the work could probably be done under simulated conditions, it is expected that most of the experimental work would have to be carried out on-site, using actual cement plant exhaust gases.

#### Short-Term Projects (0-3 Years)

- (1) A Study of Buildups Inside Circular Tubes Due to Electrophoresis and/or Thermophoresis.
- (2) Measurement of Gas-Side Fouling Factors for Design Purposes Using Typical Geometries in Representative Exhaust Gas Streams.
- (3) An Investigation of the Effectiveness of Various Cleaning Devices in Cement Plant Exhausts.
- (4) Gas-Side Fouling of Enhanced Surfaces in Cement Plant Exhausts.
- (5) The Use of Infrared Thermography to Detect Buildups in Preheaters and Kilns.

### Long-Term Projects (3-10 Years)

- (1) A Comprehensive Study of Gas-Side Fouling Mechanisms in Cement Plant Exhaust Gas Streams Including:
  - (a) Characterization of gases at high temperatures.
  - (b) Development of a well-instrumented experimental gas-side fouling probe to measure fouling rates.
  - (c) A study of all relevant particulate fouling deposition and removal mechanisms including gas composition, gas velocity, gas temperature, surface temperature, and surface material as parameters.
  - (d) A study of all relevant wet-wall deposition and removal mechanisms including gas composition, gas velocity, gas temperature, surface temperature, surface material, and dew-point or de-sublimation temperature as parameters.
  - (e) A study of all relevant chemical reaction fouling mechanisms, including the effect of fouling inhibitors, as a function of the parameters: gas composition, gas velocity, gas temperature, surface temperature, and surface material.
- (2) An Exploratory Study to Determine Gas-Side Fouling Problems Associated with the Use of Organic Rankine Cycle Waste Heat Boilers in Preheater Exhausts.
- (3) The Development of Advanced Concept Heat Exchangers to Mitigate Gas-Side Fouling in Bypass Exhausts.
- (4) Novel Techniques for Recovering Low-Grade Energy (Temperature less than 535 K) in Cement Plants by Avoiding Potential Gas-Side Fouling Problems.

### 8.3 CONCLUDING REMARKS

Heat recovery efforts in the cement industry have had an interesting history in this country. Starting around 1915 and continuing for about 50 years, waste heat boilers were used extensively to produce electricity for inplant use. However, because of relatively cheap fuel as well as fouling and other technical problems, the use of waste heat boilers fell into disfavor and the recent trend has been toward the use of suspension preheaters as a principal method of heat recovery. However, even with the use of preheaters, the exhaust gases leave the preheater at a temperature of about 645 K and hence contain considerable recoverable energy. Since most of the cement plants are presently purchasing all of their electricity for plant use, there is little need for energy which would be recovered from the exhaust gases other than that presently being utilized, i.e., heating of secondary air by the clinker cooler and drying of raw materials prior to the feed entering the kiln.

However, as energy costs continue to rise and as the nation becomes more energy-conscious, there will be an increasing emphasis on energy conservation efforts in the cement industry. Since the recuperated energy is not in great demand for plant purposes, it appears that the future push will once again be in the direction of waste heat boilers and the development of cogeneration schemes. Although steam boilers have been used exclusively in the past in cement plants, it would appear that several streams, especially the preheater exhaust gases, are ideal for the organic Rankine cycle. It is expected that steam waste heat boilers will also receive greater attention. At the same time there will be interest in recuperating the energy from the hot air exhausted from gas-to-air heat exchangers which is presently being wasted. Also, there will eventually be interest in the recovery of energy from low temperature exhausts, an area which has become synonymous with acid and water dewpoint condensation and related problems. However, in the latter cases new uses for this energy -- for example, absorption refrigeration and air conditioning systems -- would have to be found.

Whatever path is taken toward the road of heat recovery in the cement industry, there will be associated gas-side fouling, as well as other technical, problems. Although there are certain aspects of this problem which tend to be generic, there are many problems which are unique to the cement industry because of the nature of the basis process of making cement. Clearly, any gas-side fouling problems in the cement industry which can be overcome at this time will hasten to pave the way for the adoption of heat-recovery procedures in the future.



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